XX International Conference on Chemical Reactors "CHEMREACTOR-20"

ABSTRACTS

December 3-7, 2012, Luxemburg

Boreskov Institute of Catalysis of the Siberian Branch
of the Russian Academy of Sciences, Novosibirsk, Russia

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CHEMREACTOR-20

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Novosibirsk, 2012

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PLENARY LECTURES

Professor Mikhail Slin'ko Honorary Lecture

FROM NANO-PINBALL TO NANO-SNOOKER: TOWARDS PERFECT CHEMICAL REACTORS VIA FUNDAMENTAL CONCEPTS OF PROCESS INTENSIFICATION

Andrzej Stankiewicz

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The driving forces of our world are globalization, sustainability, partnership, innovation, discovery and development. The way for satisfying the increasing demand for progress, improvement, raw materials, energy and products under constrains imposed by the concept of sustainable development is a complex problem.

The control of chemical reaction pathways at molecular level presents undoubtedly the most important scientific challenge on the way to fully sustainable, thermodynamically efficient chemical processes. Minimization or elimination of waste, reduction of separation operations which are responsible for circa 40% of energy consumption in chemical and related industries and possibility for tailored manufacturing of new, advanced products - these are the most obvious advantages of a better molecular reaction control.

Factors responsible for the effectiveness of a reaction include: number/frequency of molecular collisions, geometry of approach, mutual orientation of molecules at the moment of collisions and their energy. Despite several Nobel prizes awarded for fundamental works in the area of the reaction dynamics and molecular reaction control (e.g. Herschbach, Lee and Polanyi, 1986), current chemical reactors offer a very limited degree of control of molecular-level events. In order to bring more molecules at the energy levels exceeding the activation energy threshold conductive heating is conventionally applied. However, conductive heating offers only a macroscopic control upon the process and is thermodynamically inefficient. It is non-selective in nature, which means that non-reacting (bulk) molecules heat up together with the reacting ones. Also, other elements of the reactor are unnecessarily heated up. Secondly, the conductive heating generates temperature gradients, which creates a broad Maxwell-Boltzmann distribution of molecular energy levels.

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It is clear that in order to meet the future needs of sustainable world, a new generation of chemical reactors, which I call "perfect reactors", must emerge. A groundbreaking solution in those reactors will consist in creating a reaction environment, in which the geometry of molecular collisions is controlled while energy is transferred selectively from the source to the required molecules in the required form, in the required amount, at the required moment, and at the required position.

Perfect chemical reactors can only be realized by simultaneous and multi-scale application of four fundamental approaches of Process Intensification, respectively in the spatial, thermodynamic, functional and temporal domains. To get there, a multidisciplinary research effort is needed involving not only chemistry, catalysis and chemical engineering but also the "non-chemical" disciplines such as applied physics, electronics and materials science.

The lecture is illustrated with examples of various paths towards "perfect chemical reactors" explored within the Chair of Intensified Reaction and Separation Systems at Delft University of Technology. Those paths include the use of lasers and electric fields to control molecular alignment/orientation and the local use of electromagnetic irradiation for molecular activation. New concepts of chemical and catalytic reactors based on the above alternative energy forms are presented. The addressed application areas of those new reactor concepts range from the manufacturing of green fuels and chemicals to the solving of sanitation issues in the developing countries.

Professor Mikhail Slin'ko clearly recognized the fundamental significance of mathematical modeling and computer simulations for the catalyst and reactor design. His scientific legacy includes many important publications in that area. Our quest for "perfect chemical reactors" builds on that legacy and expands its further, by introducing the physical modeling of energy fields and energy-material-medium interactions as a basis for the development of new, alternative energy- based reactor concepts.

PHOTOCATALYSIS: ENGINEERING ASPECTS OF PHOTOCATALYTIC PROCESSES

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Photocatalytic oxidation today is considered as a quite universal method for air purification from low concentrations of dangerous organic, inorganic, and biological species.

The focus of main efforts in this area is synthesis of highly active photocatalysts which are usually based on the anatase form TiO_2. Its modification by acidic treatment or noble metals deposition [1] could result in further enhancement of photoactivity. At the same time, the adsorption properties of the photocatalytic system also influence on the rate of photocatalytic oxidation especially in the low concentration range.

As it was demonstrated in the static reactor in the case of using TiO_2 supported on the activated carbon (TiO_2/AC) photocatalyst the faster removal of acetone vapor was observed (Fig. 1) [2, 3].

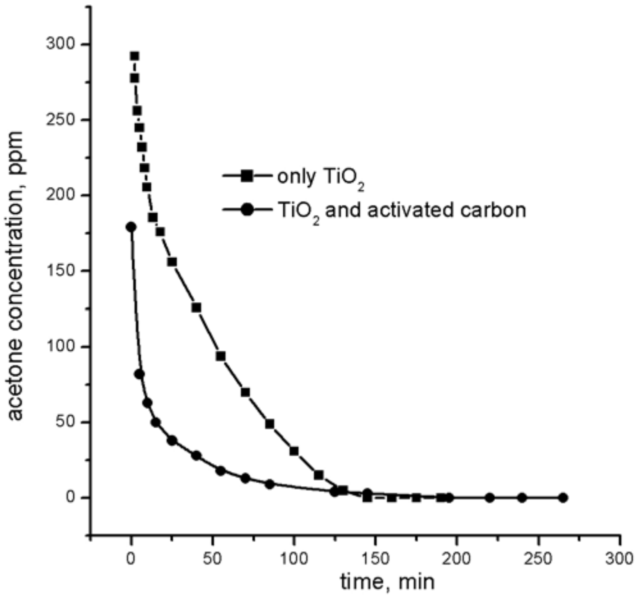

Fig. 1. Kinetic curves of acetone vapor removal by the TiO_2 and composite TiO_2/AC photocatalysts under the UV light irradiation.

Unfortunately, the rates of gas-phase photocatalytic processes alone are often insufficient to oxidize organic vapors rapidly in photocatalytic reactors. In this case the combination with other methods could increase the efficiency of photocatalysis. For example, combination of photocatalysis and plasma discharge could increase the rate of photooxidation [4] whereas the combination with gaseous H_2O_2 vapor decreases in some cases the TiO_2 deactivation when the aromatic species undergo photocatalytic oxidation [5].

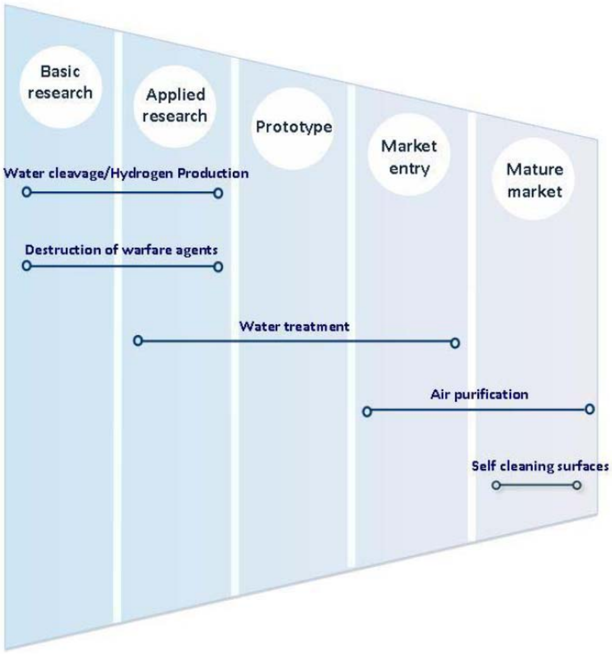

Fig. 2. Technology readiness levels for selected applications of photocatalysis

Synthesis of highly active photocatalyst is only one of the variety of problems which should be solved when the commercial photocatalytic purifiers are under development. Other problems concern mass transport limitations; improving the contaminants adsorption; influence of the contact time; optimizing the utilization of photons; deactivation of the photocatalyst and adhesion of photocatalyst onto the support as well as the adjustment of photocatalyst activity against specific contaminants and preventing the emission of byproducts [6].

Modern approach for solving these problems as well as application results in the Russian Federation and worldwide are the subject of lecture.

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ADVANCED KINETIC MODELING OF HYDROCARBON CONVERSION PROCESSES

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What is hampering today the practical implementation of advanced reactor models is a realistic kinetic modeling of the chemical process. Certainly, in hydrocarbon conversion processes the feed is generally complex and difficult to analyze and the reaction scheme may seem to be overwhelming and not amenable to rigorous kinetic modeling. The approach that has generally been chosen is to describe the feed in terms of traditional and easily accessible characteristics, like density, boiling range or Conradson Carbon number. The reaction scheme is then written in terms of a number of globalizing reactions between "lumps" with little relation to the real chemical pathways leading to the desired exit product spectrum. The kinetic model obtained from such an approach is entirely empirical and cannot be applied reliably to different operating conditions or variations in the feedstock of the process. Instead, the present paper illustrates the power of a fundamental approach which has become possible and generally applicable due to the progress in analytical means and computing power.

The first problem to be addressed is the generation of the detailed feed composition starting from its traditional characterization. This has been achieved either through a stochastic approach or by the application of the rules which govern characteristic moieties in their assembling into constitutive molecules of different nature. The latter approach will be illustrated in the talk.

The next step is the generation of the complete reaction network out of the predicted feed analysis using Boolean relation matrices and characteristic vectors. The network is gigantic and requires a fundamental description in terms of true elementary steps to be tractable. That induces the consideration of classes and subclasses of paraffins, olefins, naphthenes, aromatics and naphtheno- aromatics which distinguish between the number of substituents and the number of rings. The number of types of elementary steps in which those species are involved is surprisingly small. Within these types the single event concept, based upon transition state chemistry and statistical thermodynamics, permits extracting the structure dependency from the entropy contribution to the rate coefficient and calculate it from quantum chemical software. The remaining part of the entropy is unique for each type of elementary step and is determined from the experimental kinetic data. The enthalpy part of the rate coefficient is made unique per type of elementary step through the Evans-Polanyi free energy relationship, that involves only 2 independent parameters per type of elementary step. These are derived from the experimental data. The relationship also contains the heat of the elementary step, which is calculated from quantum chemistry. In all these calculations the symmetry numbers of the various types of elementary steps and the heats of formation are required, but the literature contains reliable information on this. The set of continuity equations for the components, to be integrated for reactor design and simulation, but also for the parameter estimation, can be reduced to 1266.This number is set by the lumping of components into Groups of Isomers (GOI) whose product distribution is at equilibrium because of the very rapid H- and Me-shifts in its constituents. Equilibrium distribution between the components is a condition for rigorous lumping. In addition, the physical properties of these components are very close. It should be stressed that this lumping in GOI's should not be considered as "late "lumping. It does not affect at all the level of kinetic description and is just a way of avoiding the integration of a gigantic set of differential equations. These coefficients are functions of temperature only and do not depend on the feedstock composition. Their values, calculated for temperature intervals of 5C, are stored in the computer memory. The primary computer output is the evolution through the reactor of 1200 GOI. Since the composition of these GOI is known the results can also be broken down into profiles of the usual commercial fractions and even into the behavior of any individual component of particular interest.

The talk will illustrate the application of the single event micro kinetic concept, linked with the Evans-Polanyi enthalpy formula to the hydrocracking of a typical Vacuum Gas Oil into fractions like gasoline, kerosene and diesel. This is industrially carried out in a 2 stage process involving a first step of hydrotreatment and a second trickle bed reactor for the hydrocracking proper. The simulation of this unit using the kinetic modeling approach outlined above is carried out by means of the ProMax software developed by BRE.

The single event approach has now been applied to processes on acid catalysts, loaded with metals like the catalytic reforming of naphtha, the fluidized bed catalytic cracking of VGO, the methanol to olefin (MTO)-process, but is applicable also to other catalytic processes involving long homologous series of hydrocarbons, encountered e.g. in polymerization. It also enables to deal in a much more systematic way with the coke formation generally associated with these processes and this will be illustrated by means of the MTO-process.

ENGINEERING & CATALYSIS CHALLENGES IN PETROLEUM REFINING

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The introduction will define the scope of the lecture and be devoted to a short multifarious overview of the refining scene today highlighting its complexity, challenges and future. In particular we will stress how evolving societal needs require new technological solutions. Because engineering and catalysis have always been tightly linked in oil refining, these two aspects will be discussed together.

We will then highlight where innovation is required in existing and classical refineries. This will be illustrated with case studies such as the gasoline/diesel balance in the FCC (Fluid Catalytic Cracking), the selective ring opening of its LCO (Light Cycle Oil) fraction, the solid acid alkylation catalysts, the problem of sulfur and nitrogen …

We will then move to the challenges associated with the increased processing of heavy ends and unconventional oils (oil sands…) as these will require major advances to improve their energy and carbon efficiencies.

Alternative and renewable feedstocks will require further innovations to make them more affordable and lower further their carbon footprint and energy efficiency. In particular, the field of GTL is now at crossroads. The large scale GTL plants need lower capital requirements to be deployed commercially and the emergence of modular GTL units for stranded oil and gas fields require the downscaling of all their unit operations. The field of biofuels brings further challenges such as the economical and “green” removal of many oxygenated compounds with minimal hydrogen consumption.

The thesis of this presentation is that, although presently seen as a mature field, oil refining can reinvent itself and further extend its reach on the basis of advances in engineering and catalysis meeting societal needs in a sustainable and affordable way.

PL-5

OLEFIN POLYMERISATION REACTORS: WHAT KIND OF PROBLEMS DO WE FACE IN OLEFIN POLYMERISATION REACTORS, AND WHAT KIND OF LAB TOOLS CAN WE USE TO STUDY THEM?

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Let us consider Figure 1, that shows the interconnection between the different characteristic length scales of the phenomena occurring inside the polymerization reactor. For example, in the case of a fluidized bed reactor, the injection of gas (and eventually liquids) will fluidize the particles in the bed. This will cause a complex flow field to develop, leading to the mixing (and perhaps segregation) of the powder. Particles can therefore be exposed to different velocity fields, and thus heat transfer conditions. The heat transfer conditions will have an impact on the particle temperature and, therefore, on intraparticle rate of polymerization and on the polymer molecular weight. Depending on temperature, molecular weight, and α-olefin content, the polymer may soften if overheated. If the mixing conditions in the particle cloud favour particle-particle contact, then the softened particles can eventually agglomerate, leading to lump or chunk formation. If this becomes serious, then bed operation can become compromised and one finds a single particle with a volume of several cubic metres!

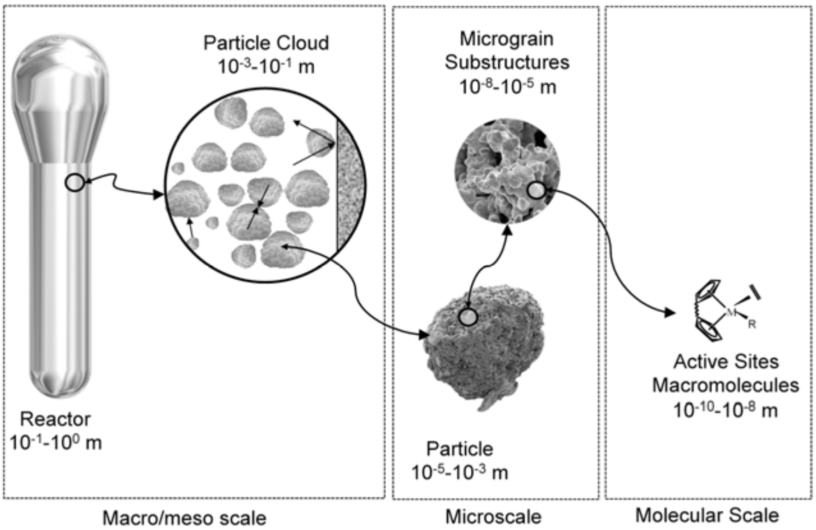

Figure 1. Rough hierarchy of length scales in an olefin polymerization process, placing the particle at the heart of events as a filter between macroscopic events on the left-hand side, and molecular events on the right-hand side

A summary of the different phenomena that might be included at each length scale is given in Table 1. It may come as a disappointment to learn that many mathematical models for industrial reactors often ignore many details. For instance, many models assume that the conditions in the polymerization reactor are uniform. This last simplification might be a good approximation for solution polymerization reactors under uniform, well-mixed conditions, but will depart from reality for supported catalysts in slurry and gas phase processes. This is because of inhomogeneous flow fields, i.e. the particles (especially in a gas phase process) are exposed to different conditions at different points in the reactor. In addition, despite years of modelling efforts, certain information is still missing in terms of writing accurate models for particle growth and the interaction of the particles with their immediate environment. Once again, if one considers Figure 1, it should be clear that without an accurate description of the particles, it is hard to model the reactor; but also that without a decent understanding of the different conditions inside the reactor it is difficult to have confidence in our reactor models.

Table 1. Description of phenomena to be modeled at different length scales for olefin polymerization reactors

Macro/mesoscale (Reactor Scale)	Microscale (Particle Scale)	Particle (Molecular Scale)
10"3 - 10 m	10"" - 10"3 m	10 m
Macromixing: reactor scale concentration and temperature gradients	Particle morphology	Polymerization kinetics:
Residence time distribution and particle size distribution	Heat and mass transfer phenomena	Microstructure, MWD, CCD, LCB
Particle interactions, aggregation	Observed kinetics, rate limiting steps	
Hydrodynamics and local velocity fields	Phase equilibrium, monomer sorption and desorption in polymer phase, diffusion	
Overall heat and mass balances		

For a number of reasons that will be discussed in the associated conference, one of the major stumbling blocks in developing an accurate description of the particle, and the impact of the reactor environment on the particle is a lack of appropriate experimental tools. To overcome (at least in part) this challenge, our group has adapted a specially conceived packed bed stopped flow minireactor (2.5 mL) suitable for short (down to 0.1 s) pulsed gas phase polymerizations, and another adapted for solution or slurry polymerizations. In the gas phase reactions we have studied the influence of temperature, gas solid relative velocities, olefin concentration and bed particle properties on the nascent polymer properties (Tm, crystallinity, MWD) and on the short time activity profile of different metallocenes supported on silica particles. We have proved that there is a strong evolution of activity and polymer properties in the first 5 s of reaction for all the tested conditions. In addition the activity and the MWD time dependent profiles are very sensitive to the fluid/solid relative velocities suggesting that heat transfer plays a fundamental role in the first seconds of the reaction. Finally the MWDs show unexpected time dependence in the first seconds proving that complex interactions between transient phenomena are at play at the reaction start-up. This talk will therefore focus on an overview of existing polymerization reactors (with the emphasis on gas phase systems), and on how we might solve some oft he numerous remaining problems with specially adapted laboratory reactors.

MODERN BIOFUELS: COMBINATION OF CHEMISTRY AND BIOTECHNOLOGY

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The author analyzes the grounds of new contemporary processes to produce biofuels by conversion of biomass and organic waste. Resource potentials of technologies for production of biofuels from renewable feedstock are quite high and surpass those of the present-day oil-and-gas industry. A major raw produce potential of biofuel industry is polymeric carbohydrates, polyphenols, solid and organic polymeric wastes. A basic chemical process for biofuel production is the reactions of dehydration and hydrophobization of monomeric carbohydrate-containing feedstock ("hydrocarbons from carbohydrates").

Depolymerization. Studies analyze the ground processes leading to production of soluble carbohydrates of hexose and pentose nature from biomass. This includes:

- Enzymatic hydrolysis by new celluloselytic and hemicelluloselytic enzyme complexes.
- Acid hydrolysis at experimental and industrial levels.
- Mechanochemical pretreatment of cellulosics and hemicellulosics with a concurrent catalytic hydrolysis of polymers.
- Transfer of biopolymers into solution with a subsequent hydrolysis of the polymer solutions.
- Use of ionic liquids for amorphization and hydrolysis of cellulose and hemicellulose.
- Creation of novel classes of hydrolysis catalysts based on polypeptides – the models of hydrolytic enzymes.

Transformation of monosaccharides into fuel. Heterogenous catalytic processes. Classic biotechnological processes for production of biofuels are based on the use of microbiological conversion of a dissolved feedstock into bioalcohols (ethanol, butanol), methane and hydrogen.

Novel processes are examined, based on the use of heterogenous catalysts in the form of immobilized cells – fuel producents. Studies analyze the processes of self-immobilization of cells (biogas), the genetic engineering modifications of producers leading to self-formation of granules of fuel producers as well as the development of new effective and economically applicable heterogenous catalysts based on cryoimmobilized cells.

Merits of the system based on heterogeneous catalytic processes are shown.

- Higher rates of the processes and higher yields of the end products.
- Waste decrease.
- A notable simplification of the end products purification.

Merits of heterogenous catalytic producers are shown by the examples of ethanol, butanol and acetone productions.

New biofuels. Bioketals. Studies examine a novel process for biofuel production by dehydration and hydrophobization of carbohydrates due to ketals production reaction via interaction of polyols (glycerol, pentose, hexose with acetone). Study likewise analyses the chemical and technological grounds of the process and the parameters of the produced gasoline-soluble components as agents raising the octane number and the phase stability of motor fuel.

Biophotolysis of water. The studies analyze the systems for water photodecomposition to obtain separately hydrogen and oxygen by use of immobilized cells of microscopic algae and microbial producers of molecular hydrogen. The “artifitial leaf“ system of solar energy transformation to produce hydrogen is examined.

Biooil. The studies examined:

– The novel processes for conversion of biomass and polymer materials in the form of solid domestic waste into a liquid carbon–containing fraction (biopetroleum). The developed methods of flash-pyrolysis are based on new physical principles of rapid heating of the solid phase of initial biopolymeric or polymeric material. The work presents a complete analysis of the reaction products proceeding from the initial feedstock; the energy and fuel parameters of biopetroleum have been obtained. The promises of application of the novel flash-pyrolysis for conversion of solid domestic waste are analyzed. The overall global trends for production of biofluels from renewable raw produce and dynamics of biofuel industry development compared to that of the global oil complex are shown.

PL-7

NEW CATALYSTS AND REACTOR DESIGNS FOR THE HYDROGEN ECONOMY

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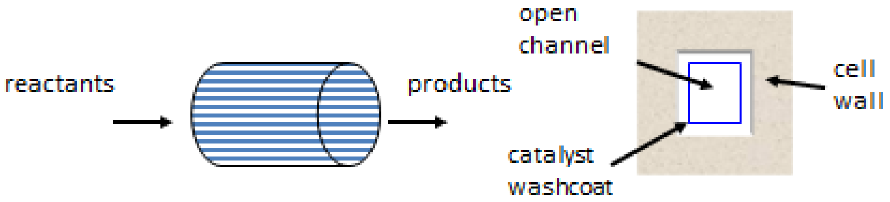
New catalyst formulations and reactor designs are necessary to meet the expanding use of hydrogen based fuel cells. Catalytic fuel processing will require a small footprint and low pressure drop since infrastructure fuels (e.g. natural gas and LPG) will be reformed for the fuel cell to power homes, commercial buildings, schools and hospitals, etc. These systems must operate unattended safely and reliably in the user facilities. To meet varying power demands, precious metal washcoated catalysts on monolithic structures, similar to those successfully used for the last 35 years in the automobile catalytic converter, are a logical choice [1]. The figure below lists some of the advantages of precious metal monolith designs.

General Characteristics of Precious Metal Catalysts on Monoliths

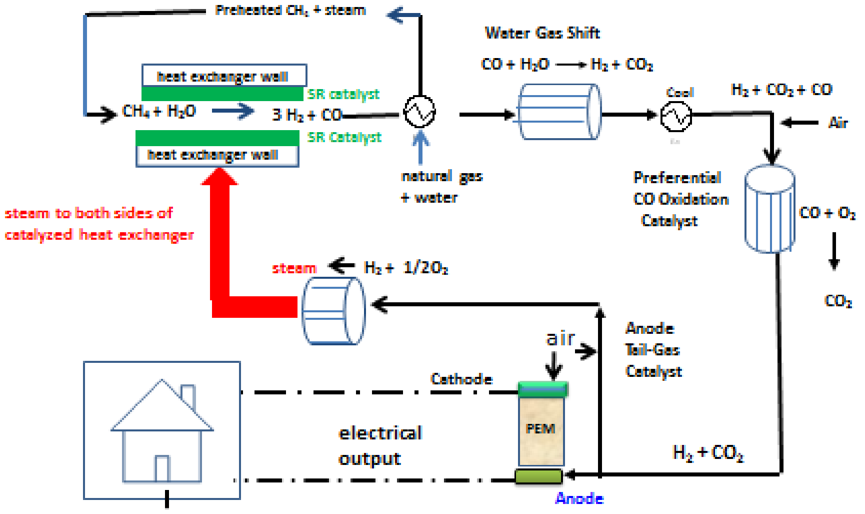


- Monolith structures are available with geometric surface areas up to 5 m^2/liter (1200 cells/in^2 or 181 cells/cm^2)
- Up to 90% open frontal area are available to give low pressure drop
- Precious metal washcoating technology produces adherent and stable catalyst layers resistant to deactivation during thermal cycling
- Precious metal catalysts have high activity densities permitting thin layers of washcoat to be used
- Rapid response to transient operation especially for washcoats on heat exchangers is achieved
- Precious metal recovery is available and is an important part of the overall economics of the system

The figure below shows one arrangement for processing natural gas to fuel cell quality H_2 using washcoated monolithic structures. Of particular importance is the use of catalyzed heat exchangers for effective steam reforming of desulfurized natural gas; an endothermic process. By depositing a highly active precious metal catalyst on the walls of a heat exchanger high H_2 production rates can be achieved by enhanced heat transfer relative to the commercially used tubular packed beds of Ni catalysts. We have demonstrated an increase in throughput (space velocity) of about 5 times that of a traditional packed bed [1].

PL-7

Natural gas steam reforming for PEM fuel cells



To further enrich the process stream of hydrogen a new precious metal water gas catalyst on a conventional ceramic monolith is used to reduce the CO to about 1%. The CO is further reduced to < 5 ppm in the preferential oxidation reaction (PROX) using a highly selective precious metal containing washcoat on either a ceramic monolith or heat exchanger if heat is to be recovered.

The endothermic heat required for steam reforming is provided by a ceramic supported precious metal catalyst which combusts the tail gas and directs the heat to the shell side of the heat exchanger.

Today's lecture will include a discussion of catalysts, processes, reactor designs, potential aging issues and duty cycles for natural gas reforming for residential combined heat and power, distributed power using LPG and portable power by reforming methanol water mixtures.

A brief discussion of a newly developed catalyst and process for steam reforming sulfur-containing fuels will also be discussed.

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KEY-NOTE LECTURE

COMPETITIVE DIFFUSION OF GASES IN A MICROPOROUS CATALYST BED USING A SLICE SELECTION PROCEDURE

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Introduction

We presented in a previous paper [1] a new NMR imaging technique which can be used for following the diffusion and adsorption of a gas in a microporous bed [2]. The sample is displaced vertically, step by step, relative to the detector during the adsorption of the gas; the detector is a very thin coil. The bed is assumed to consist of *n* very thin layers of solid, and the region probed is limited to each layer; so the variation of the concentration of gas absorbed at the level of each layer is obtained as a function of time. Experimental conditions, mathematical modelling and analytical solution giving the concentration profiles have been described in [2]. This technique allows the determination of: - the gas diffusion coefficient profiles D_{intra} and D_{inter} against time *t* at each level of the zeolite bed; - the intercrystallite concentration profiles, $C\ (z,t)$, versus time *t* for different values of the position *z* in the bed; - the concentration profiles, $Q(t,X,z)$, in zeolite crystallites located at different positions *z* in the bed, and *X* in the crystallites, for different times *t*.

But the most interesting thing is that this technique is able to visualize directly the co-diffusion of several gases. Indeed, in contrast to the classical ^{1}H NMR imaging, it gives a signal characteristic of the adsorbed gas. It can therefore provide directly, at every moment and at every level of the crystallite bed, the distribution of several gases competing in diffusion and adsorption.

Experimental results

As a first example we show the co-diffusion of benzene and hexane gases in equilibrium with its liquid phase, at 25°C, through a bed of ZSM5 (length 15 mm) initially under vacuum. Figure 1 shows the sample-holder tube which is moved vertically, up or down, opposite the very thin detector. The two gases begin to diffuse in the zeolite when the glass partition is broken.

KN-1

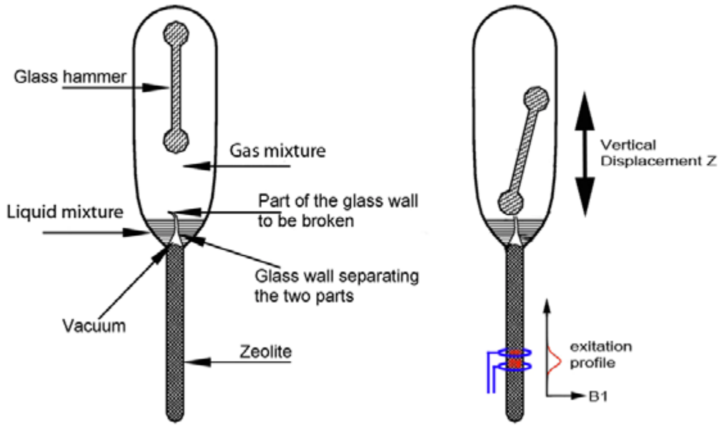

Figure 1: left: Sample-holder bulb containing the liquid phase in equilibrium with the gas phase; right: Schema of the narrow zone monitored.

Figure 2 compares the evolution, as a function of time, of the benzene and hexane concentrations, at different levels of the sample from a height of 6 mm down to 14 mm. It reveals particularly well, under the chosen experimental conditions, the negative effect of benzene on the diffusion of hexane, and this at every moment.

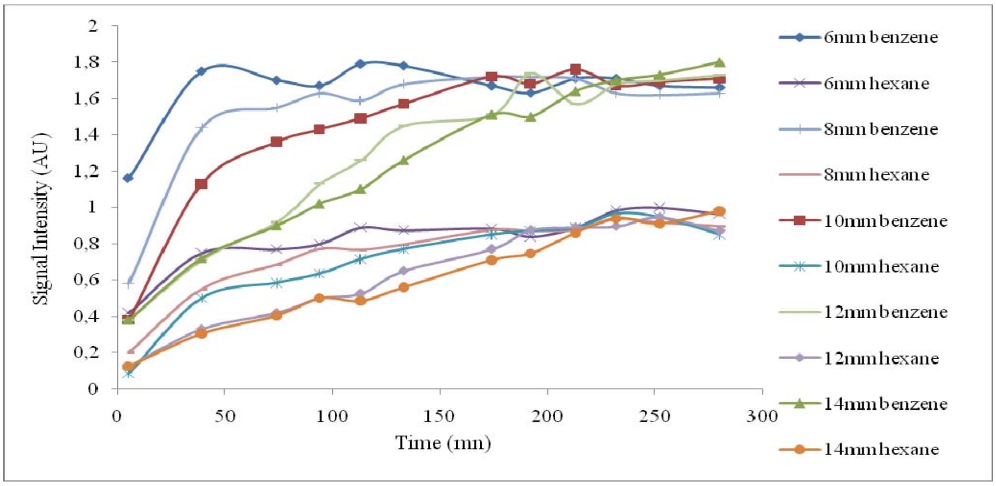

Figure 2: Time variation of the benzene and hexane concentrations at different levels of the sample.

Conclusion

The choice of the two diffusing gases, benzene and hexane, is not what is most important. The main result is the possibility, for the first time, of following at every moment the concomitant distribution of several gases co-diffusing in a porous solid.

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INTEGRATED APPROACH TO REDUCTION OF MOBILE DIESEL EMISSIONS

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Diesel engines are essential for moving commercial goods and people, at the same time generating significant emissions of regulated pollutants such as particulate matter (soot), nitrogen oxides, hydrocarbons and carbon monoxide. Increasingly stringent regulations have resulted in highly effective emission control systems being introduced in US, EU and Japan, to be followed in the future by developing markets.

The mobile aftertreatment systems are closely integrated with engines and vehicles. The engine and vehicle design, load, driving cycles, environmental conditions – all that affects the parameters of the exhaust gas and the performance of the system which, in turn, affects vehicle operation through pressure drop, need for active system management, maintenance requests, etc. Increasing adoption of technologies targeting lower CO_2, such as hybrid powertrain and waste heat recovery, brought about additional complexity of the powertrain and, as a consequence, of aftertreatment interaction with other vehicular systems.

The automotive industry is using systematic product development methodologies to deal with challenging design targets. A top-down path from the high-level requirements analysis to concept formulation and definition of components is followed by bottom-up process of integration of components and subsystems into final vehicle. As complexity increases, virtualization of the development process becomes essential. For emission control, this means the development and implementation of chemical process simulation tools.

A state-of-the-art diesel aftertreatment system carries out three major functions:

Soot filtration typically takes place in a d*iesel particulate filter* (DPF), a monolith with porous walls that serve as filtration media. The collected soot is removed via passive oxidation by NO_2 or high-temperature (550-750°C) combustion during periodic active regeneration events.

NOx reduction is done, depending on application, using a *selective catalytic reduction* (SCR) with ammonia generated from decomposition of urea injected as a 32.5 % aqueous solution, or using storage and periodical reduction of NOx by hydrocarbons in a *Lean-NOx trap* (LNT).

Oxidation of hydrocarbons and CO is carried out by a *diesel oxidation catalyst* (DOC) coated with Pt or Pt/Pd. The DOC also oxidizes NO into NO_2 to facilitate passive soot oxidation and improve the performance of SCR catalyst or LNT. It also enables active DPF regeneration by burning injected fuel.

KN-2

Active NOx control systems and DPF regeneration require intelligent control algorithms that continuously estimate states of the system (i.e. temperature and storage levels: NH_3 in SCR catalyst, NOx in LNT, soot and ash in DPF) and initiate precise injection of urea solution (SCR) or hydrocarbons (LNT and DPF). The algorithms process inputs from multiple sensors to calculate the reaction rates using maps or simplified kinetic models. Diagnostics of and adaptation to catalyst deactivation are important issues in the control system design.

The pressure to reduce the system cost and size drives the development of multifunctional components, such as

- DOC/DPF combination that comprises DOC coating in the front portion of the DPF
- SCR/DPF that loads SCR washcoat is into the pores of the DPF walls

The SCR/DPF combination is especially interesting both due to its cost savings potential and the complexity of the catalyst design and operation: optimization of the porous structure of the substrate, interaction of soot reactions with SCR chemistry, control of urea solution injection and DPF regeneration, etc. Recent experimental and modeling studies have contributed to the understanding of the new catalyst behavior and resulted in models that successfully simulate the system performance in transient driving cycles.

Implementation of SCR technology requires a sub-system that converts urea solution into uniformly distributed ammonia in front of the SCR catalyst. This is achieved by the analysis of distribution of sizes and velocities of urea solution droplets exiting the injector, simulation of spray interaction with the gas flow and surfaces in the exhaust system walls, followed by CFD simulation of the performance system design modifications.

Still, conversion of urea solution to ammonia gas limits the low-temperature performance of SCR system, the problem being amplified in advanced powertrains that reduce energy waste and thus decrease the exhaust gas temperature.

One way of dealing with colder exhaust gas is through optimization of system architecture and component design. Another solution is implementation of systems that generate NH_3 gas off-line from solid (ammine complexes or ammonium carbamate) or liquid (urea solution) media. In all cases, NH_3 generation requires the source heat energy. Simulation of the entire powertrain or vehicle is instrumental in identification of available energy sources.

In summary, current diesel aftertreatment systems are complex chemical plants combining catalysts, sensors and auxiliary components designed and integrated to meet challenging performance requirements under highly transient operating conditions. The task of the system design and integration in a vehicle requires extensive use of virtual engineering tools built on the foundation of reliable and accurate catalytic reactor models.

DESIGN OF PROCESSES FOR VALUABLE CHEMICALS PRODUCTION FROM BIOMASS

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Catalysis and reaction engineering are the key disciplines in a successful conversion of molecules from biomass to end products. The interactions of kinetics, mass transfer and flow pattern in the processing of biomass should be considered. Chemical analysis and precise kinetic measurements combined to mathematical modeling are the basic elements in the scientific development of the reaction engineering of biomass conversion. Advanced kinetic concepts, such as cluster kinetics, size-dependent kinetics can be combined to the models of porous catalyst particles and chemical reactors.

In the very past, biomass, especially wood, was used as a source of many chemicals, typical examples were ethanol, turpentine, regenerated fibres (cellulose xanthate), polymers (e.g. cellulose acetate) and explosives (e.g. cellulose nitrate). However, the access to relatively inexpensive crude oil and natural gas led to a decline of wood-based chemical industry. Now, the concept of biorefinery is making a breakthrough. It implies that biomass will be used as raw material, instead of natural gas, crude oil or coal. This development creates big challenges for science and technology, particularly for chemistry and chemical engineering. New catalysts and processes are needed, included new reactors, new separation technologies, new reaction media. Still, the metholodogical aspects of chemical engineering, and particularly chemical reaction engineering remain, and they will be used for the design of biorefineries.

The aim of the lecture to illustrate, how the central concepts of chemical reaction engineering can be applied to the transformation of biomass to chemicals and fuel components.

The real challenge is the description of complex mixtures originating from biomass. The reactions of cellulose and hemicellulose have similarities (e.g hydrolysis of macromolecules as well as transformations of sugar monomers), while the reactions of lignin fractions and various extractives are very different from those of cellulose and hemicelluloses. On the other hand, if a selective fractionation procedure is applied to biomass, the issue becomes easier from a reaction engineering viewpoint: extractives are removed first from woody biomass by leaching with an organic solvent, hemicelluloses can be separated in the next step by hot water extraction and finally, either cellulose is hydrolyzed or lignin is dissolved.

The future kinetic approach to biomass conversion will be based on the reactivities of functional groups in the modeling of complex mixtures. Advanced lumping techniques will be needed, as they are nowadays applied to hydrocarbon mixtures originating from fossil sources. A lot of physical properties for biomass components should be measured experimentally, such as densities, viscosities, heat conductivities and polarities of solutions containing biomass. These properties are needed in the modelling of chemical reactors, particularly diffusion phenomena in bulk liquids and in porous catalyst layers.

Since many of the molecules appearing in biomass are large, the role of internal diffusion is prominent as heterogeneous catalysts are used for chemical transformations. This requires very precise mathematical modelling of simultaneous reaction and diffusion in porous structures. Two issues are of particular importance: the pore structure of the catalyst and the design of the catalyst layer itself. In order to enhance the diffusion of the reactive molecules to the active sites of the catalyst, catalysts with large pores should be preferred. Molecular modeling is of great help to indicate, whether a reactant can fit to the pore structure of a proposed catalyst.

In order to diminish the diffusion resistance, to improve the effectiveness factor, the catalyst layer should be thin, which could be achieved in the conventional slurry reactor technology with finely dispersed catalyst particles, applying egg-shell type catalyst particles or structured reactors, such as monoliths, fibres and solid foams. The decision on the reactor technology should be based on precise experimental measurements and detailed mathematical modeling.

Many tools exist for a precise description of the reaction kinetics mass and heat transfer effects and they are applicable for biomass conversion, but catalyst deactivation is a dilemma in the treatment of biomass. For instance deactivation of decarboxylation catalysts is very strong mainly due to the decarbonylation reaction proceeding simultaneously. Deactivation in hydrogenation catalysts is quite severe because of various impurities presence. Catalyst deactivation should be prevented or at least diminished in order to design economically feasible processes based on biomass conversion.

Many of the catalysts developed for the treatment of fossil feedstock do not work in an optimal way when they are exposed to components from biomass. Fundamental research in the reaction mechanisms and catalyst deactivation, including the use of single crystals and other model catalysts are needed to reveal the chemical and physical reasons for deactivation. In this way, better catalysts can be developed in the future. Active, selective and durable catalysts can be used in advanced – and sometimes expensive – reactors, such as monoliths, foams and fibre reactors. The work requires a close collaboration between chemists, physicists and chemical engineers.

Finally, it has to be stated that there should not be any specific chemical reaction engineering of biomass, but the general principles of chemical engineering should be applied to molecules and mixtures originating from biomass. Without a precise knowledge of chemistry and detailed mathematical modelling of kinetics, thermodynamics, transport phenomena and flow pattern, a successful biomass conversion cannot be achieved.

ORAL PRESENTATIONS

SECTION I

Advances in Chemical Reactors Fundamentals

Chemical Reactions Kinetics
Fundamentals of Chemical Reactors Simulation
Heat & Mass Transfer in Chemical Reactors
Hydrodynamics and CFD Studies in Chemical Reactors

OCM PROCESS AND REACTOR DESIGN: A PHYSICAL CHEMIST LOOK

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Oxidative coupling of methane (OCM) to higher hydrocarbons, including light olefins (ethylene) is a promising way to involve abundant and relatively inexpensive methane resources into the production of basic intermediates for chemical and petrochemical industry [1]. Although this reaction was discovered more than 30 years ago and for a certain period (in mid-1980's - early 1990's) had been very extensively studied, up to now it has no practical implementation, despite it is very attractive, especially for plants of relatively low unit capacity. In this work the major features of the OCM reaction and typical OCM catalysts are discussed in terms of how physicochemical characteristics of the reaction system affect the overall process and reactor design.

It is almost generally accepted that the primary OCM product is ethane, which is formed via the recombination of two free methyl radicals generated during the reaction of methane molecule with active oxidizing surface site according to the scheme:

$$[O]_S + CH_4 \rightarrow [OH]_S + CH_3^{\bullet} \qquad (1)$$

$$2\,CH_3^{\bullet} \rightarrow C_2H_6 \qquad (2)$$

Below it is shown how particular technical solutions are dependent on the further elaboration and development of the OCM reaction description.

1. Redox nature of catalytic action.

The H-atom abstraction from the methane molecule can proceed via several alternative mechanisms. Without going into the intimate details, one can definitely say that the overall process is oxidative. It was also clearly demonstrated that most of typical OCM catalysts can produce reaction products via interaction with methane in the absence of gaseous oxidant (e.g. O_2, N_2O, etc.) at the expense of strongly bonded oxygen species (surface or bulk). This allows one to carry out the OCM process in one of two alternative regimes:

(i) continuous ("traditional catalytic") and

(ii) periodical (alternated reduction/re-oxidation of solid oxide).

Besides economical (capital intensity) and safety (formation of flammable/explosive mixtures) factors, there are several physicochemical characteristics of the particular oxide system which determine the alternative choice:

- OCM product selectivity in different regimes;
- ease of the target product separation;
- amount of active oxygen available for a single redox cycle;
- kinetics of reduction (with methane and ethane) and re-oxidation steps;
- heat production (consumption) in separate stages.

Such characteristics require and integrated consideration based on a thorough study that utilizes appropriate experimental methods.

2. Product formation pathways and OCM reaction kinetics.

The scheme (1)-(2) shows that the overall OCM process is allocated in two reaction zones - on the catalyst surface and in the volume of gas phase. The escape of the reaction to the latter causes a formation of numerous secondary radicals which, in their turn, are involved into a complex reaction network, that includes both homogeneous and heterogeneous transformations. The kinetic description required for a rational OCM reactor design should satisfy two conflicting demands:

(i) be full enough to reflect a complexity of the real reacting system;

(ii) be concise and precise enough to fit with requirements of reactor modeling (e.g., in the framework of CFD simulations) and optimization.

Such model can be composed based on the trade-off between an analytical description that accounts a redox character of catalytic active sites (Mars-van-Krevelen-type kinetics) and a detailed ("micro-kinetic") description taking into account the key homogeneous steps responsible for the product selectivities.

The approaches to the gathering of appropriate experimental information, to the development of rational kinetic model and to their utilization in the process/reactor design are discussed. In particular, a petroleum gas chemical processing flowsheet based on the OCM reaction as a core module will be presented.

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OP-I-2

MoS_2 NANOPARTICLE PRECIPITATION IN TURBULENT MICROMIXERS

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Advanced nano-materials such as transition metal sulfides (Mo,W) [1], have shown some promise due to their contribution in reducing friction and enhancing protection against wear, when incorporated in full lubricant formulations in a stable way. MoS_2 nano-particles have been synthesized through a wet chemical synthesis in aqueous solution with ammonium molybdate, citric acid and ammonium sulfide [2]. Since MoS_2 precipitation is a fast process, it derives that the rate and extension of mixing is determining for the process outcome: because of their ability to achieve high mixing efficiencies necessary in the precipitation process, VORTEX micromixers (Fig. 1) are being investigated for this application: this micromixer has four inlets, of 1 mm in diameter, and a reaction chamber (highlighted in red) of 4 mm in diameter and 1 mm in height. The product is discharged in a 2 mm diameter duct, perpendicular to inlet radial flow. Primary NP with a 50-500 nm diameter were produced: they appear as loosely agglomerated NP clusters, which can then be disengaged so that primary NP can express their intrinsic lubricant action (Fig. 2) [1].

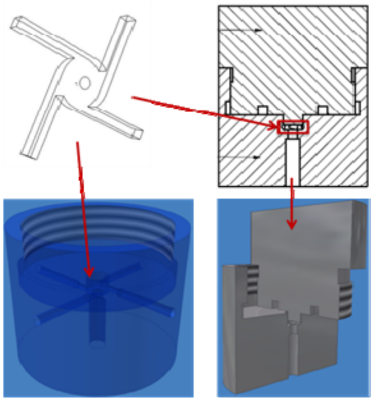

Fig. 1. VORTEX rendering.

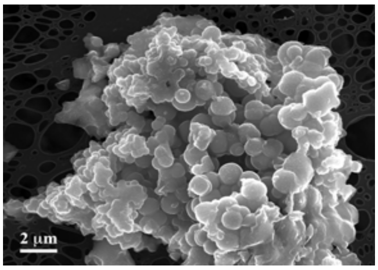

Fig. 2. MoS2 SEM for a 2 ml/min inlet flow rate.

The aim of this work is to study the fundamental aspects of NP formation process in the VORTEX micromixer, by means of a precipitation model based on CFD developed for MoS_2 NP formation. The flow field in the VORTEX micromixer was simulated by using a Reynolds Average Navier–Stokes equations (RANS k-ε and k-ω for transitional flows) and Large Eddy Simulation (LES) turbulence models, and flow field predictions were validated against experimental data of μ-Particle Image Velocimetry [3], used to measure the velocity fields of the same micro-fluidic device. The of radial velocity prediction, at different planes perpendicular to the mixing chamber axis, are extremely accurate (Fig. 3 refers to an inlet Reynolds number of 93, reached for 20 ml/min in each inlet channel, corresponding to 1740 if referred to the mixing chamber diameter).

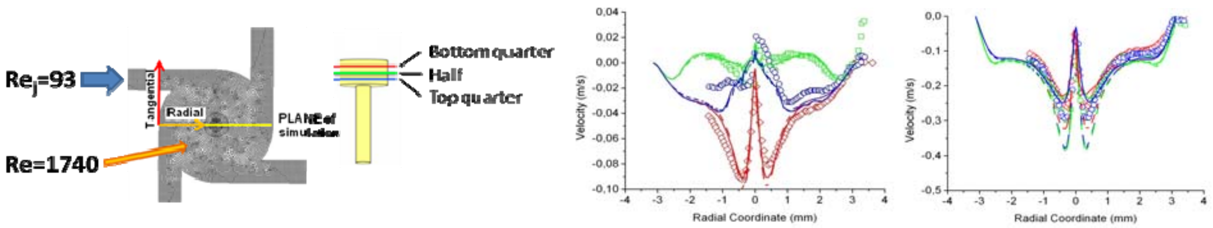

Fig. 3. Micromixer flow filed: a) radial and b) tangential velocities. Experimental (dots), LES simulation (solid line), k-ω simulation (dashed).

The precipitation model solves the micromixing and the population balance equation (PBE), and employs the precipitation kinetics based on the super-saturation of the reacting species, from which the steps of nucleation, growth and aggregation depend, and consequently the particle size distribution, particle morphology and composition. Accurate description of this model is found in [4]. The micromixing model DQMOM-IEM has been used to model the reactants transport equations in the 2 environments (Mo-citrate and sulfide solutions) [5]. The PBE describes how the population of particles evolves due to nucleation, molecular growth and aggregation. The QMOM approach solves the PBE by tracking the evolution of the lower-order moments of the particle size distribution (PSD). Fig. 4a shows results of mean mixture fraction of reacting environments for Re=93, which is directly related to the turbulent viscosity (k-ε) in the micro-mixer (Fig. 4b). Preliminary results of NP diameter (synthesis conditions fully detailed in [2]) can be seen in Fig. 4c, which is the global effect of NP nucleation (which occurs where super-saturation is reached, which is the highest in the yellow regions of mean mixture fraction Fig.4a), growth (depending on the residence time) and agglomeration (related to the turbulence of the system and thus to NP collisions).

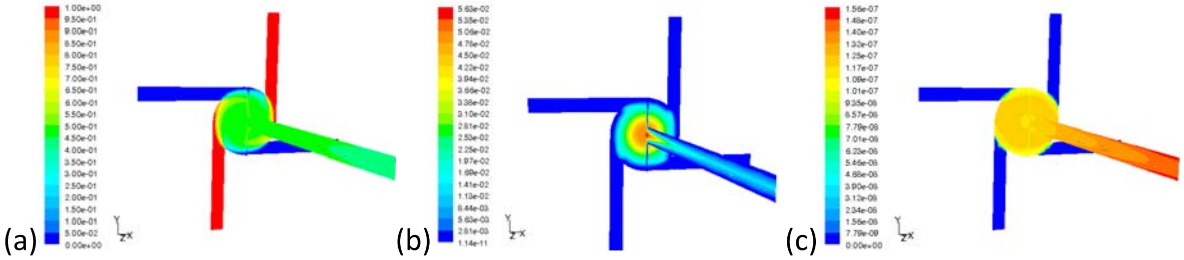

Fig. 4. Computed values of a) mean mixture fraction (red: Mo-citrate complex, blue: sulfide); b) turbulent viscosity, kg/ms; c) MoS_2 NP diameter, m.

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OP-I-3

MICROKINETIC FOR TOLUENE TOTAL OXIDATION OVER $CuO-CeO_2/Al_2O_3$

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The catalytic total oxidation of volatile organic compounds (VOCs) is generally considered to be an effective method for reducing the emission of pollutants in the environment [1]. Conventional catalysts, based on noble metals (Pt, Pd) supported on Al_2O_3, are successfully used to eliminate VOCs by total oxidation. Transition-metal oxides, such as copper, cobalt, manganese and chromium, are also known to be active combustion catalysts [1]. They are less active at lower temperatures but show comparable activity at higher temperatures and present high catalyst loading capabilities. CuO was reported equally effective as Pt for the combustion of n-butanol and methyl mercaptan [2] and for the total oxidation of ethanol [3]. Larsson and Andersson found excellent performance for the conversion of CO, ethyl acetate and ethanol over CuO_x/Al_2O_3 [4]. Moreover, CuO was the most active transition-metal oxide of those tested for the catalytic combustion of toluene with γ-Al_2O_3 as support [5]. CuO promoted by CeO_2 was observed to show better catalytic performance for total oxidation than a supported CuO catalyst [5,6].

The mechanism of oxidation of VOCs over transition-metal oxide catalysts, was established to follow Mars and Van Krevelen type redox cycles [7]. The first step consists of the reactant oxidation using catalyst lattice oxygen which will be replaced, in the second step by dioxygen. In addition, adsorbed oxygen species are also active in hydrocarbon oxidation catalysis [7]. The respective roles and nature of the active oxygen species, e.g. adsorbed oxygen species acting as electrophilic oxygen, and lattice nucleophilic oxygen, in catalytic combustion are not fully clarified and need further investigation.

In this study a binary mixed-oxide $CuO-CeO_2/\gamma$-Al_2O_3 catalyst has been investigated and compared with the corresponding single metal-oxide compounds CuO/γ-Al_2O_3, CeO_2/γ-Al_2O_3. The structure of the catalysts was investigated by means of high resolution electron microscopy (HRTEM), selected area electron diffraction (SAED), X-ray diffraction (XRD) and X-ray absorption near edge structure (XANES). A transient response technique with millisecond time resolutions, so called Temporal analysis of products (TAP), was used to investigate the reaction network.

Alternating pulse and isotopic labeling experiments indicate that the catalytic total oxidation of toluene over CuO-CeO_2/γ-Al_2O_3 proceeds through the following sequence [8]: parallel adsorption of toluene on the catalyst surface, step 1; simultaneous abstraction of H from the methyl and the phenyl group, step 2 and 3; abstraction of the methyl carbon atom, step 4, followed by destruction of the aromatic ring, step 5. Two types of oxygen are directly involved in the oxidation of toluene: adsorbed oxygen and weakly bound surface lattice oxygen.

The binary metal oxide, CuO-CeO_2/γ-Al_2O_3, has an improved performance in toluene total oxidation in comparison with its corresponding single oxide components CuO/γ-Al_2O_3 and CeO_2/γ-Al_2O_3 due to the presence of a $Ce_{1-x}Cu_xO_{2-x}$ solid solution. During catalysis, two redox couples Ce^{4+}/Ce^{3+} and Cu^{2+}/Cu^{0+} coexist within this phase. Separate bulk CuO particles have significantly lower catalytic activity.

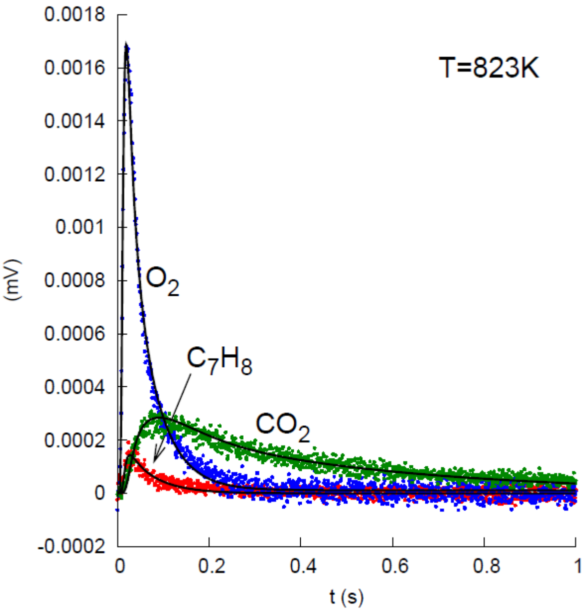

Figure 1. CO_2, C_7H_8 and O_2 responses at 823K corresponding to a $C_7H_8/O_2/Ar$ single-pulse experiment. (·) Experimental responses; (-) responses calculated with parameter estimates.

A microkinetic model accounting for the above was developed. The kinetic parameters were estimated to be statistically significant and to have a sound physical-chemical meaning. Fig. 1 shows the good correspondence between the experimental and calculated transient CO_2, C_7H_8 and O_2 responses.

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METHANE DRY REFORMING BY TRANSIENT KINETICS STUDY

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Ceria-zirconia oxide solid solutions with impregnated precious metals exhibit high efficiency and stable performance in dry reforming of methane [1-2]. Rare earth metals with variable valence ($Sm^{3+/4+}$, $Pr^{3+/4+}$) incorporated into these systems stabilize the structures of pure ceria-zirconia system and increase the oxygen mobility through the formation of oxygen vacancies which prevent catalyst deactivation by coke deposition [3]. Methane dry reforming was extensively studied by many researchers but the mechanism of this process over CeO_2-ZrO_2 solid solutions has not been clarified yet [2, 4]. This work presents the results of transient kinetics study for the mechanism of methane dry reforming over Ni + Ru catalysts supported on ceria-zirconia oxide solid solutions doped with rare earth metals.

Nanocrystalline fluorite-like oxides $(Sm,Pr)_x(Ce_{0.5}Zr_{0.5})_{1-x}O_2$ were synthesized using Pechini route and promoted by Ru and Ni via impregnation or by the introduction of promoter salts into a solution of polymer precursors [5]. Temporal Analysis of Products (TAP) reactor was applied to study the adsorption properties and reactivity of the catalysts [6]. Transient kinetic experiments were performed in a quartz micro-reactor placed in a high vacuum chamber (10^{-4} –10^{-5} Pa). The number of molecules admitted during the pulse experiments amounted to 10^{13} – 10^{14} molecules/pulse ensuring a Knudsen flow regime throughout the experiment. To identify the reactive surface species and the individual reaction steps, a series of pulses of CO_2, $CH_4 + CO_2$, and CH_4 with variation of time lag between pulses were performed. The influence of the pretreatment procedure (oxidation, reduction) and temperature on kinetic characteristics was studied.

Pre-oxidized catalysts showed no activity for dry reforming at TAP conditions. Only after catalyst reduction in H_2, formation of CO from CO_2 and CH_4 was observed. In case of CH_4 admission to the catalyst, hydrogen was also produced. For Ni+Ru/$SmPrCeZrO_2$ catalyst in a steady state, the amount of CO formed in a pulse of $CH_4 + CO_2$ was found to be equal to the sum of CO in the individual pulses of reaction mixture components. Therefore, the stages of activation and conversion of the components of the reaction mixture are independent and proceed via simple red-ox mechanism (Fig. 1): CO_2 dissociates on support sites (most probably, oxygen vacancies) with formation of CO and oxygen atom which is further transferred along domain boundaries to metal sites where CH_4 molecules are transformed to CO and H_2. This conclusion was confirmed by pump-probe TAP experiments with $^{13}CO_2$ showed that CO is produced separately from CO_2 and CH_4 without direct interaction of methane with carbonaceous species. H_2 and $^{13}CO_2$ pump-probe experiments indicated the absence of direct interaction of carbonaceous species with H_2. The reverse WGS reaction proceeds via redox mechanism at the given condition. The transient kinetic data are described quantitatively with statistically sound kinetic models and physicochemical meaningful parameters.

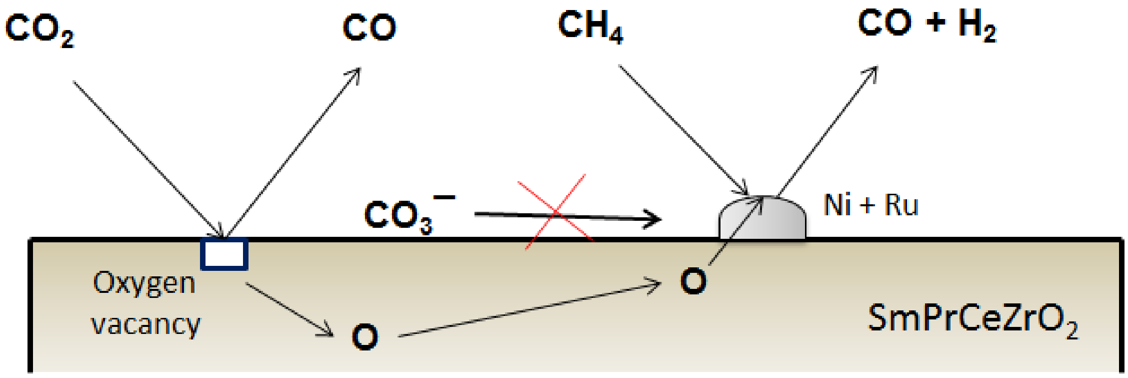

Fig. 1. Scheme of methane dry reforming over Ni+Ru supported on $SmPrCeZrO_2$.

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OP-I-5

DEVELOPMENT OF THE INTEGRATED MEMBRANE REACTOR FOR HYDROGEN PRODUCTION AND STEADY-STATE ISOTOPE TRANSIENT KINETIC ANALYSIS SYSTEM, TECHNICAL ASPECTS

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The hydrogen economy has enormous societal and technical appeal as a potential solution to the fundamental energy concerns of abundant supply and minimal environmental impact. Generation of pure hydrogen represents a critical technology component for power generation by PEM fuel cells in a variety of mobile and stationary power applications. Hydrogen is conventionally produced by steam reforming of hydrocarbon fuels followed by a water gas shift reaction and hydrogen separation and purification.

The group of researchers from National R&D Institute for Cryogenics and Isotopic Technologies - ICIT Rm. Valcea start to develop of the integrated membrane reactor for hydrogen production and steady-state isotope transient kinetic analysis (SSITKA) system. The work disclaims some efforts of researcher from National Hydrogen and Fuel Cell Center in order to develop above mentioned system. The experimental work is focused on optimizing of the membrane reactor and SSITKA functions.

The aim of presentation is a new approach of physical and chemical investigation which occur in the main components of the technological chain of a hydrogen production base on methane catalytic steam reforming. The use of stable isotope tracers as a new investigation tool – Steady-State Isotope Transient Kinetic Analysis - was first applied and developed in the ‘80s, but it potential was not fully brought into play. Therefore the target of the group of researchers is to put into practice this analysis as a new instrument to understand the mechanism of the physical and chemical processes within the catalytic methane steam reforming membrane. SSITKA is considered to be an ideally suited method to investigate the gas-surface processes and especially the ones driven by catalyst and membrane.

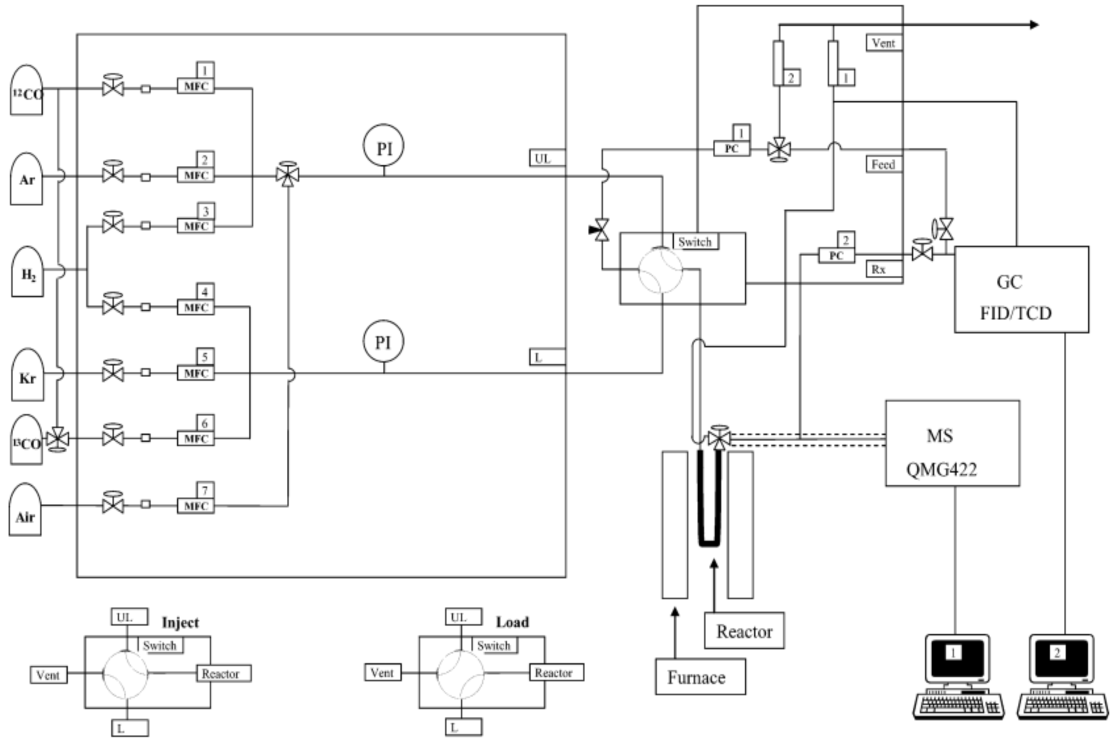

Fig. 1. The diagram of membrane reactor for hydrogen production and steady-state isotope transient kinetic analysis (SSITKA) system.

Activities are planned to be developed onto two distinct levels – one is related to the investing concerning fundamental knowledge for the processes which occurs in the main components of the hydrogen production and the second is a technological development of such integrated system using the information achieved and taking into account the existing expertise in the field.

The goal of the SSITKA investigations is to find a model that describes the rate of the reaction as a function of variables that define the physical or chemical processes. The kinetic analysis of SSITKA response data is based on non-linear regression data. Parameter estimation will be based on model fitting to experimental data of gas phase concentrations since the surface concentrations are usually unobservable quantities.

Acknowledgements

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SYNTHESIS OF DIMETHYL CARBONATE FROM THE CARBONYLATION OF METHANOL AT HIGH PRESSURE CONDITIONS: KINETIC CONSIDERATIONS

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Since the industrial revolution the energy consumption has exponentially increased, which led to an excess of CO_2 concentration in the atmosphere [6]. This excess of CO_2 is the major cause of global warming and became one of the most discussed topics in the scientific community. The sequestration of CO_2 is pointed out as a solution for the reduction of CO_2 emissions, either by the mineral carbonylation or by its use as feedstock. Indeed, CO_2 can be used as a building block for organic products, such as salicylic acid, urea or organic carbonates [2].

Organic carbonates are considered green chemicals due to their low toxicity, being important compounds able to replace volatiles organic compounds as solvents [5].

From an economic point of view, the principal organic carbonates are: dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC) and glycerol carbonate (GC). Among them, dimethyl carbonate (DMC) is especially important because it can be used as methylation and carbonylation agent, replacing the hazardous dimethyl sulphate and phosgene, respectively [9].

Dimethyl carbonate can be produced by the carbonylation of methanol. The major drawback of this reaction is the low DMC yield reached at equilibrium conditions and the low reaction rate caused by the high stability of CO_2. Hence, several authors have been studying new catalysts to improve the reaction rate: ZrO_2 [7], CeO_2 [11], ZrO_2-CeO_2 [8], H_3PO_4/V_2O_5 [10], $CuCL_2$/activated carbon [3], $Co_{1.5}PW_{12}O_{40}$ [1], Ga_2O_3/ZrO_2-CeO_2 [4]. In spite of the amount of studies available in literature, none of them presents a kinetic model to describe this reaction, which will be of extreme importance in order to implement a sustainable DMC production process.

In this work, a kinetic model was developed in order to describe the carbonylation of methanol using CeO_2 as catalyst. Different kinetic experiments were performed; the effect of relevant parameters, such as pressure, temperature, CO_2/MeOH ratio and mass of catalyst was studied. The reaction equilibrium was determined and compared to the one predicted by thermodynamic models.

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TRANSIENT STUDIES OF REACTION KINETICS OVER THE SOLID CATALYSTS WITH LATTICE OXYGEN MOBILITY

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Dynamic methods for studies of catalytic reaction kinetics are well known to provide more detailed and reliable kinetic information as compared to conventional steady-state methods. Experimental and numerical tools permit to extract the data about the reaction mechanism and surface state elucidating catalytic kinetics required for design purposes and process optimization. These approaches were developed successfully for the gas-solid systems in which the catalytic properties are determined mainly by chemical transformations on the catalyst surface [1].

At the same time, the modern studies have revealed that for the oxide catalysts the lattice oxygen mobility can play an important role in the catalytic system behavior, affecting transient regimes as well as activity, selectivity and stable performance of catalysts [2, 3]. This work aims at the numerical studying of transients and obtaining of kinetic data for complex catalytic reactions taking into account lattice oxygen mobility in the oxide catalyst.

In our studies the mathematical description of isothermal catalytic process in the flow reactor was used which includes the mass balances of components in the gas phase and at the catalyst surface as well as in the near surface layers of the catalyst lattice. The numerical studies with software developed were performed for two cases:

- the theoretical analysis was carried out with model kinetic scheme,
- transient behavior of CH_4 dry reforming over Pt/CeZr oxide catalyst was analyzed.

At first, the computational runs were fulfilled for the model reaction occurring by redox mechanism, and transient regimes were considered with 3 levels of catalytic activity, including the reaction conditions of CH_4 partial oxidation as an example of fast reaction. The following results were obtained:

- It has been demonstrated that numerical analysis allows a lot of information on the time dependence of species concentrations in the gas flow, on the active surface and in the bulk of catalyst to be derived.

- Inherent time scales and its ratios were estimated for main factors controlling the catalytic properties and stability: catalytic reaction stages, including the deactivation steps; lattice oxygen mobility; oxygen surface transformation, etc.
- It has been shown that the possibility exists to evaluate from transient curves such quantitative characteristics of catalyst structure as the number of surface active sites and near surface layers of crystalline lattice involved in the oxygen exchange with the surface sites.

These results were verified by simulating the transient behavior of CH_4 dry reforming over Pr-doped Pt/CeZrO catalyst. The studies were performed for the process parameters corresponding to the experimental transients of the reaction mixture with CH_4 concentration of 7% vol. and CH_4:CO_2 ratio 1:1 fed to the oxidized catalyst at temperature 750°C and short contact times (4.7-15 ms). The factors controlling different transient periods and character of transient curves were elucidated, and the rate values of bulk and surface oxygen diffusion as well as quantitative characteristics of the state of the catalyst surface and oxygen non-stoichiometry in the surface/bulk layers were obtained. Moreover, data processing allowed the discrimination of kinetic schemes supposed to be realized. The kinetic parameters of the stages of selected reaction mechanism were estimated, experimental and modeling data being in a good agreement.

Hence, transient studies of reactions on the oxide catalysts with oxygen bulk diffusion were shown to be an effective tool for elucidation of the reaction kinetics on the base of detailed data about reaction mechanism.

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THE INFLUENCE OF SOLIDS' PROPERTIES ON THE CAKE FORMATION IN FILTRATION OF PLANT OILS SUSPENSION

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Filtering of suspensions is one of the major technological processes in production of various chemicals and foodstuff. This paper is focused on determining the efficiency of cake filtration after catalytic hydrogenation of plant oils in a slurry reactor. Proper filtration of the catalyst secures high quality of the products and may increase the unit capacity. A number of industrial filtering materials for separation of hydrogenated oils from dispersed powders of catalysts have been studied in this paper. Experimental results and modeling data related to the influence of solids' properties on the cake formation in precoat filtration of plant oils suspension through candle-type filters are discussed.

In all experiments, commercially available fat blend was used as a medium; it was produced by catalytic hydrogenation of a mixture contained palm oleine, sunflower oil and palm stearine. Melting point of the medium was 40°C, and viscosity was 7.4 MPa·s at 80°C. Dispersed materials that were tested are as follows:

- Dust-free mesoporous carbon material *Sibunit*, fraction 50-200 mcm;
- Supported catalysts 0.5%Pd and 1%Pd on *Sibunit*, fraction 100-200 mcm;
- Ni-containing commercial hydrogenation catalyst Pricat-9908;
- Kieselguhrs Celatom® FW-70 and Celite-545, fraction 45-105 mcm.
- Alumina Puralox® SCCA--150/200, fraction 150-200 mcm.

Particles sizes distribution of the powdered materials has been measured by means of Laser Diffraction particle size Analyzer SALD-2101 (*Shimadzu*). Specific surface of filters has been investigated by means of scanning electronic microscopy (SEM), device JSM-6460LV (*JEOL*), at the accelerating voltage of 15-20 kV. SEM images of some powders are shown in Fig.1.

To simulate the conditions that correspond to the filtering modes close to industrial ones in scale 1:250, we used the laboratory pilot plant equipped with the vertically arranged candle filter. Commercially available weaved filter screens *Amafilter* of wire thickness 0.36-0.26 mm and nominal retention size 120 mcm were used. Experimental procedure consisted in continuous recycle-mode filtering the suspension of fines in the melted fat medium through the screen filter. Experimental data showed strong influence of the parameters of precoat filtration on the filtration time of suspensions during multiple cycles of filtration.

The mathematical model of filtering the dispersed material through a porous filter screen was proposed; and the opportunity of its application to the prediction of cake filtration performance was shown.

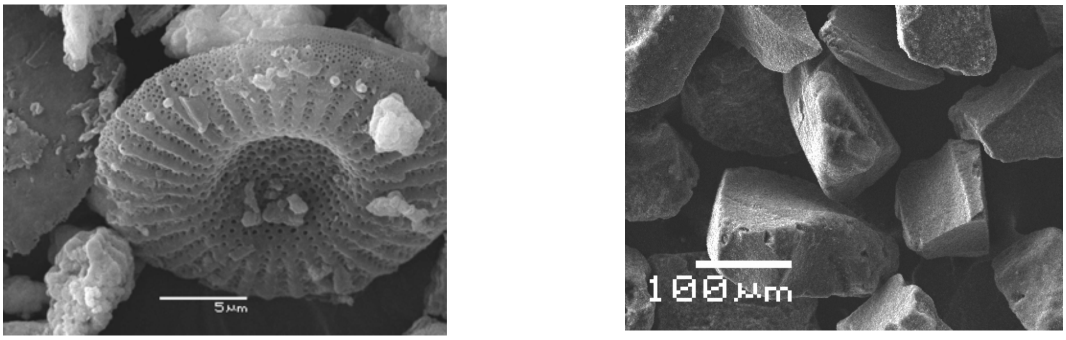

Fig. 1. SEM images of Ni-containing commercial catalyst (left) and Sibunit (right).

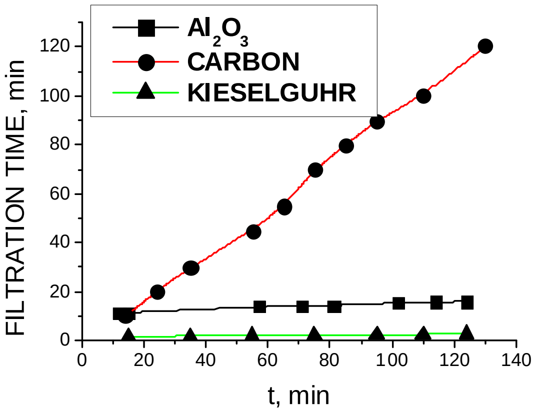

Fig. 2. Filtration time of Alumina, Sibunit and Kieselguhr suspension in melted fat vs. precoat filtration time

Experimental data shown at Fig. 2, describe the time of a filtration of melted fat for industrial plant conditions in view of the correction, considering real pressure drop on the filter ΔP, measured during experiments on laboratory setup. As one can see, filtration time of Kieselguhr and alumina are small enough, whereas filtration time of carbon suspensions increases owing to plugging up in pores of a filter screen.

OP-I-9

MATHEMATICAL MODELING OF REGENERATION OF COKED Cr-Mg CATALYST FOR FREONS PRODUCTION

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In production of ozone-safe chladones (R-134a, R-125 etc.) by gas-phase hydrofluorination of chloroethylenes the catalysts, containing chromium (+3) and fluorides of metals of Group II, are used. Catalyst deactivation in these processes is caused by coking. During its regeneration by oxygen it is important to prevent the catalyst overheating, which may results in the sintering of active component, and as a result, irreversible loosing its activity. In industrial processes with such a problem, the knowledge of the regeneration kinetics and catalyst bed dynamics are necessary for optimal design of the reaction-regeneration cycles.

As a rule, an industrial regeneration is carried out at high temperature, where the process behavior can be intermediate between the situations, where the chemical reaction or diffusion is the rate-controlling step. Therefore, the kinetic equation should be valid in a wide range of operating variables. So, the intrinsic kinetic parameters should evaluate as well as parameters of diffusion or mass-transfer limitation.

The aims of the present work were to study the catalyst regeneration kinetics and to develop optimal regimes of the chromium-magnesium-fluoride catalyst regeneration in an adiabatic reactor.

Regeneration of the catalyst bed is an unsteady-state process. Moreover, in every catalyst section along a bed height, oxygen concentration and gas temperature “instantaneously” adjust to variations of coke concentration and catalyst temperature, hence they are quasi-stationary. With respect for this, the two-phase mathematical model was used [1,2].

Model parameters, such as reaction rate constant, heat of reaction, reaction order, diffusion coefficient, activation energy, and coke composition, were determined from the experimental data obtained in the differential reactor and corrected by mathematical modeling.

Oxygen is fed into the catalyst pellet by mass transfer. Under quasi-stationary regime, the rate of mass transfer is equal to the rate of combustion in the pellet. The mass transfer coefficient β in the region of internal diffusion is a variable value, because the area of coke burning r_c moves from the pellet surface to its core. In addition, the catalyst porosity ε decreases on sintering, which change the value of surface through which mass transfer occurs ($3\varepsilon (1 - \varepsilon)/R_z$, cm^2/cm^3). For this reason, the finite expression for the mass transfer coefficient can be written as:

$$\beta = \frac{3600\, D_E}{(R_z - 0.95 r_c)} \frac{3}{R_z} \in (1-\varepsilon)\,,$$

where R_z – radius of a catalyst pellet, cm; D_E – diffusion coefficient, cm^2/s; ε – porosity of a catalyst bed; $\in\, = V_\Sigma\, \rho_z$ – porosity of a catalyst pellet; V_Σ – pore volume, cm^3/g; $\rho_z = \rho_k /(1 - \varepsilon)$ – pellet density, g/cm^3; $r_c = R_z\ (g / g_o)^{1/3}$ – radius of coke burning zone in a catalyst pellet, cm.

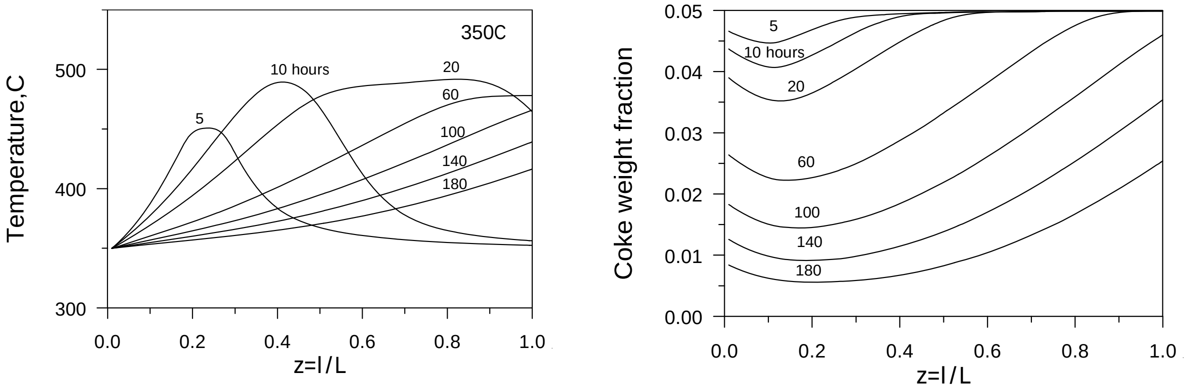

Figure. Temperature and coke concentration profiles at the different time. Pellet sizes are 8x12 mm.

Analysis of the process occurring in the catalyst bed shows that coke burning proceeds in the region of strong diffusion limitations. This is confirmed by DTG and TG analysis data.

On heating the fine-grained sample in air, coke is completely burnt out at 350-470°C. Whereas, coke burning on the catalyst pellet proceeds much longer, at the same heating rate. Moreover, because the process of oxygen diffusion into the catalyst pellet is limited, an increase in temperature does not result in an increase in the rate of coke burning.

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OP-I-10

MODELING AND CONTROL OF AN EXOTHERMICAL REACTION

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Temperature control in a batch process with an exothermal reaction is still a challenge in the chemical industry.

Batch processes are extremely important in the chemical process industry, their main applications being in the production of specialty chemicals, polymers, or bio products [1]. Also, batch reactors are significantly used in studies of reaction kinetics and thermal effects modeling [1].

In case of strongly exothermic reactions carried out batchwise, the heat removal capacity provided by the standard cooling jackets or internal coils may be too small to keep the reacting mass at the required reaction temperature [2].

It is difficult working with highly exothermic reactions under conditions where heat transfer is limited, not only for safety questions but also because the rise in temperature usually leads to an increase in the formation of secondary products as well as catalyst, products or reactants degradation.

In heterogeneous catalytic process an unexpected temperature increase can produce hot spots inside the catalyst bed and on the tube wall [3] and since the activation energy associated with catalyst deactivation is frequently higher than the activation energy of the desired reaction, hot-spots exceeding a certain maximum reaction temperature must be avoided [3].

One way of controlling the heat release rate is by using semi-batch reactors where the control of the dosing rate of one of the reactants provides an additional way to control the process [2]. Moreover, the accumulation of the reagents may be minimized and therefore, in case of deviation from the normal operating conditions, turning off the dosing can stop the process [2]. In theory, this means the elimination of risk of runaway reactions [2]. In a realistic case, it is not always possible to avoid accumulation [2]. Furthermore, to discern between safe and critical values of accumulation inside the reactor is not easy and hence, fixing critical accumulation limits can become arbitrary [2].

Nitrobenzene hydrogenation in a non-isothermal reactor is used as case study. Nowadays, aniline is mostly produced by the reduction of nitrobenzene (Figure 1), which is produced from the nitration of benzene in a mixture of sulfuric and nitric acid. The reduction of nitrobenzene to aniline is strongly exothermic and generates - 536.6 ± 5.9 kJ/mol [4].

The fact that the exothermic reaction has to be first heated and then when the reaction starts has to be very quickly cooled is a problem, because the conventional feedback control does not begin until after the controlled variable deviates from the set point [5] and that can be to late.

A generic cascade control for an exothermically catalytic reaction has been developed. This paper focuses on a batch process where the temperature control is made by an oil bath witch controls the heating/cooling coils.

The nitrobenzene reaction rate and reactor temperature were fitted to the experimental data (Figure 2 and 3, respectively).

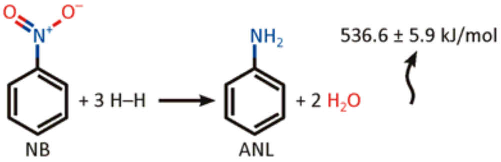

Figure1 - Hydrogenation of nitrobenzene to aniline.

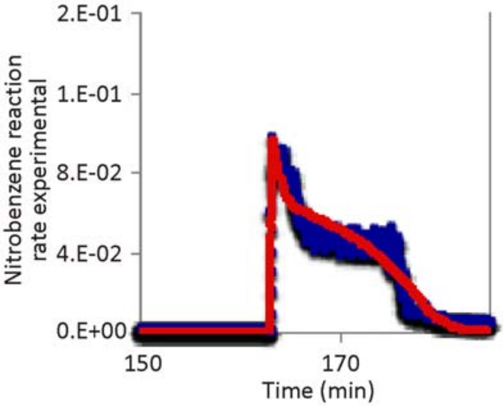

Figure 2 - Nitrobenzene reaction rate fitting.

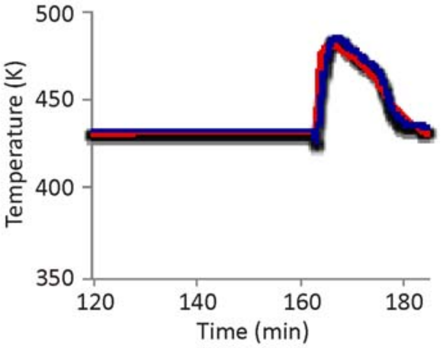

Figure 3 - Fitting of reactor temperature.

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OP-I-11

AUTOCATALYTIC GAS - PHASE PROPANE DEHYDROGENATION FOR LIGHT OLEFIN PRODUCTION

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The main products of the propane dehydrogenation in tube furnaces are methane, ethylene, hydrogen and propylene. Ethane, acetylene, butane, butene, divinyl are registered in smaller quantity. We have realized a gas-phase pyrolysis of propane under conditions of a wall - less reactor described in the articles [1-3]. The continuous CO_2 - laser was used as an energy source in this reactor. The products composition of propane dehydrogenation was founded to be similar to the one obtained in the pyrolysis furnaces. Yields of products for moderate conversions may be presented by a semiempirical expression:

$$C_3H_8 \rightarrow 0{,}53CH_4+0{,}52C_2H_4+0{,}44H_2+0{,}42C_3H_6+0{,}04C_2H_6+0{,}01C_4H_{10}+0{,}003C_4H_6.$$

Modern mechanisms of propane dehydrogenation include from forty to few hundreds of elementary stages [4]. However, using of the generally accepted kinetic schemes did not give a satisfactory description of the experimental data for high conversion of the propane.

A compact kinetic scheme of propane dehydrogenation was a result of our work. The radicals generation for a radical – chain mechanism of propane dehydrogenation was the result of propane dissociation to methyl and ethyl radicals in this scheme. Ethylene appearance in the reaction mixture emerges a competitive channel for the radicals generation $C_3H_8 + C_2H_4 \rightarrow C_3H_7 + C_2H_5$ [5]. The activation energy of this reaction is lower than in the previous one. But ethylene can turn into biradical form of a triplet stage with high reaction ability via colliding with other molecules [2]. The activation energy of the reaction for ethylene biradical formation $^{\cdot}C_2H_4^{\cdot}$ is 253 kJ/mol.

Ethylene and methane, propylene and hydrogen are produced in pairs in chain propagation reactions. Ethylene and methane formation was realized in a cycle with a lead methyl radical:

$$CH_3 + C_3H_8 \rightarrow CH_4 + C_3H_7$$
$$C_3H_7 \rightarrow C_2H_4 + CH_3$$

The reactions with leading radical H form the cycle of a propane reduction to propylene and hydrogen:

$$H + C_3H_8 \rightarrow H_2 + \text{iso-}C_3H_7$$
$$\text{iso-}C_3H_7 \rightarrow C_3H_6 + H$$

The percentage of propylene in the reaction mixture decreases in the cycle of its transformation to a propyl radical, which is decomposed to acetylene and methyl radical:

$$C_3H_6 + CH_3 \rightarrow CH_4 + C_3H_5$$

$$C_3H_5 \rightarrow CH_3 + C_2H_2$$

Ethane, butane, butene, divinyl presented in smaller quantity in the reaction mixture are produced in other cycles which were determined too. The final scheme includes 5 cycles and this scheme consists of 15 elementary stages.

In whole, the scheme represents autocatalytic mechanism of the propane pyrolysis, which has an autocatalytic route with respect to ethylene:

$$C_3H_8 + C_2H_4 \rightarrow 2\ C_2H_4 + CH_4$$

The developed kinetic scheme of the propane dehydrogenation describes most accurately the experimental results of the pyrolysis in the tube furnaces and in our experimental reactor.

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RFBR 12-08-00871-A

OP-I-12

A BUBBLING REACTOR TO STUDY WATER SPLITTING UNDER PHOTOCATALYTIC SYSTEMS AND ITS MODELING TO INVESTIGATE THE REACTION KINETICS

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Currently, production of hydrogen, a fuel with remarkable properties, through sunlight-driven water splitting appears to be a promising and appealing solution for storage of solar energy from a renewable source [1]. Water decomposition using sunlight on semiconductor photocatalysts has been extensively studied since the pioneering work on a photo-electrochemical cell conducted by Honda and Fujishima in 1972. Moreover, a widely studied approach to the make light-driven water splitting reaction consists in separating the functions of light harvesting and conversion from fuel-forming catalysis. As this is concerned, Cobalt has emerged in the past five years as the most versatile non-noble metal for the development of synthetic H_2- and O_2-evolving catalysts. Such catalysts can be further coupled with photosensitizers to generate photocatalytic systems for the water oxidation half reaction (the most challenging one) or to produce directly light-induced hydrogen from water [2].

Particulate photocatalytic systems are frequently used to study the half reactions of water splitting for H_2 or O_2 evolution in the presence of sacrificial reagents. This type of study has the advantage of being much simpler and less expensive to develop and use than photoelectrochemical cells, as well as it is particularly suited to determine whether or not a given catalyst satisfies the kinetic and thermodynamic requirements for the water splitting reaction [3]. Batch reactors are generally used for this purpose. In such systems cumulative O_2 or H_2 evolution data is discontinuosly analysed versus time. In this work we present the development of a reactor system to measure continuosly the evolution of gases, with a high precision. Figure 1 illustrates the reactor designed and implemented to measure gaseous oxygen evolution, composed by a quartz cylinder, hermetically closed, with total volume 190 mL and containing 100 ml of solution, into which Ar flows at a constant rate of 5 Nml/min and bubbles into the liquid phase, which is kept homogeneous through a magnetic stirrer. Inside the reactor, pressure (P) and temperature (T) are maintained constant at 1.06 atm and about 20°C, through the use of a pressure back regulator and a water cooling jacket. The reactor has a glass window for illumination with simulated visible light from a 450W Xenon arc lamp, using a Newport heat absorber filter (model FSQ-KQ2). The oxygen concentration (C_{O2}) in the outgoing gas mixture is measured every minute through a micro gas chromatograph (Varian 490-µGC) equipped with a Molsieve 5A column of 10m and a micro-TCD detector. From these values, the actual oxygen flow $\Phi(O_2)$ is calculated, and cumulative O_2 production was thus determined. However, no information on the real reaction rate occurring in the liquid phase was available: to this end, we have developed a comprehensive mathematical model (based on O_2 formation at the catalyst surface, then diffusion at the dispersed gas bubble interface, and finally mixing with the stagnant gas in the pocket on the top of the liquid surface), able to retrieve the actual O_2 or H_2 evolution reaction rate from recorded data, in order to study the chemical kinetics of the photocatalytic system. To validate the model, a Co_3O_4 catalyst supported on a mesoporous silica (MSU-H), noticed to be active for the water oxidation reaction under visible light [4], was tested using a three-component system composed of: (i) the catalyst, (ii) the Ruthenium complex $Ru(bpy)_3^{2+}$, acting as photosensitizer, (iii) a sacrificial electron acceptor, $S_2O_8^{2-}$. The kinetics of the reaction have been studied by varing both catalyst quantity and buffer solution, which is used to maintain constant the ph of the solution. Figure 2 reports the set of data obtained ($\Phi(O_2)$ flow as a function of time), when the amount of the Co_3O_4 catalyst was varied, and the total quantity of O_2 evolved that was calculated for every case.

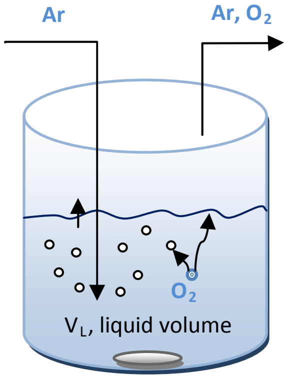

Figure 1: Schema of the reactor

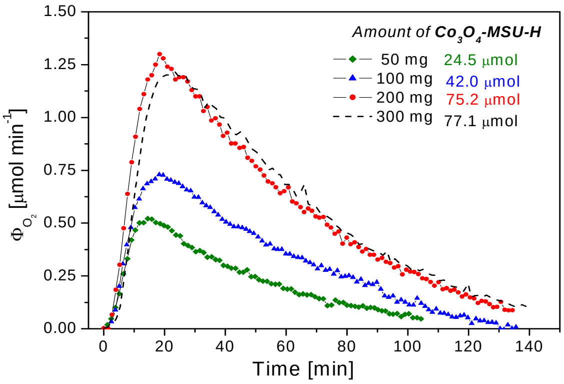

Figure 2: Oxygen flow at different

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OP-I-13

FIXED BED REACTOR FOR THE FORMALDEHYDE PRODUCTION: THE EFFECT OF NON-UNIFORM RADIAL HEAT TRANSFER

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Production of industrial chemicals is influenced by fluctuations in the market demand. At a chemical plant, the production capacity and consumption of raw materials may change a lot depending on the market situation. For widely used flow- type multi-tubular reactors, variations in raw gas feed can provoke critical regimes, and for highly exothermic processes - even runaways.

In the present work, we study reasons of occurrence of critical reactor regimes on the example of a large-scale process of formaldehyde production at one of the industrial enterprises and propose possible preventing measures.

The production of formaldehyde in this study is carried out in a multi-tubular fixed bed reactor by means of oxidizing the methanol to formaldehyde over metal oxide catalyst. This reaction is exothermic; heat withdrawal is done by the high boiling organic heat transfer fluid circulating between the tubes.

The performance analysis of the flow-type multi-tubular reactor is based on an extended continuous 2D model of heat and mass transfer. The model considers the variation of the gas linear velocity along the tube's radius and the dependence of the radial and the axial thermal conductivity on the gas linear velocity in the tubes and on the parameters of the dispersion medium.

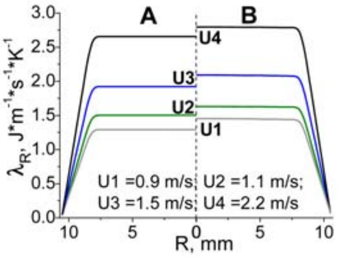

Fig. 1. Radial profiles of λ_R in the "h.s."(**A**) and inlet (**B**) of tube at various U

It is established that a decrease in production capacity accompanied with decrease in gas flow feed in the reactor leads to a decrease in the gas linear velocity, which in its turn, decelerates the heat transfer expressed by effective coefficient of heat conductivity λ_R (fig. 1). The study of the reactor's mathematical model considering non-uniform radial heat transfer has exhibited the dependence between the decrease in gas flow feed and the elevation of maximal temperature in the "hot spot" ("h.s.") of the catalyst layer (fig. 2). On a real-world multi-tubular reactor, we observe that these changes and irregularities of stream distribution can lead to critical operating regimes.

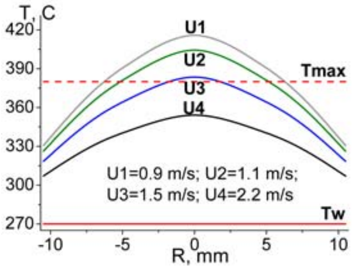

Fig. 2. Radial T-profiles in the "h.s." of tube reactor

OP-I-14

COMPUTATIONAL ISSUES CONCERNING HYDRODYNAMICS OF REFORMING REACTORS

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Radial flow reforming reactors are widely used in industrial productions due to low hydrodynamic resistance of catalyst bed as compared to axial flow reforming reactors [1].

Calculations of reactor flow dynamics imply solution of adjoin problems for heterogeneous media:

1) stream of crude gas flow in exempt reactor parts (collectors);

2) stream of crude gas flow in porous medium of fixed-bed catalyst.

Turbulent flow in collectors of reactors is described by equation Navier-Stokes, averaged in terms of Reynolds (RANS model), while in catalyst beds it is described by motion equation of non-linear filtration law [2].

We propose pass-through calculations method to solve this problem. In that event system of motion equations assumes generalized form as follows:

$$\rho\frac{dv_i}{dt}=-\frac{\partial p}{\partial x_i}+\frac{\partial}{\partial x_j}\left[-\frac{2}{3}\mu_\varepsilon\frac{\partial v_k}{\partial x_k}\delta_{ij}+\mu_\varepsilon\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}\right)\right]-\left(\zeta_1+\zeta_2\left|\vec{v}\right|\right)\rho v_i \qquad (1)$$

$$\frac{\partial\varepsilon\rho}{\partial t}+\frac{\partial\varepsilon\rho v_i}{\partial x_i}=0 \qquad (2)$$

Where: $\zeta_1=150(1-\varepsilon)^2\upsilon/(d_p^2\varepsilon^2)$, $\zeta_2=1{,}75(1-\varepsilon)/(d_p\varepsilon)$ – coefficients of Ergane resistance law, ε - bed porosity, p,ρ - mixture pressure and density, v_i - velocity components, μ_ε - effective viscosity factor, d_p - catalyst grain size, υ - kinematic viscosity of mixture.

Conditions of conjugation at the interface are obtained from equations (1) and (2) by standard method [2, 3]:

$$\left(p+\frac{\rho\left(v_1{}^2+v_2{}^2+v_3{}^2\right)}{2}+\left[\frac{2}{3}\mu_\varepsilon\cdot div\vec{v}-2\mu_\varepsilon\frac{\partial v_n}{\partial n}\right]\right)_-=\left(p+\frac{\rho\left(v_1{}^2+v_2{}^2+v_3^2\right)}{2}+\left[\frac{2}{3}\mu_\varepsilon\cdot div\vec{v}-2\mu_\varepsilon\frac{\partial v_n}{\partial n}\right]\right)_+ \qquad (3)$$

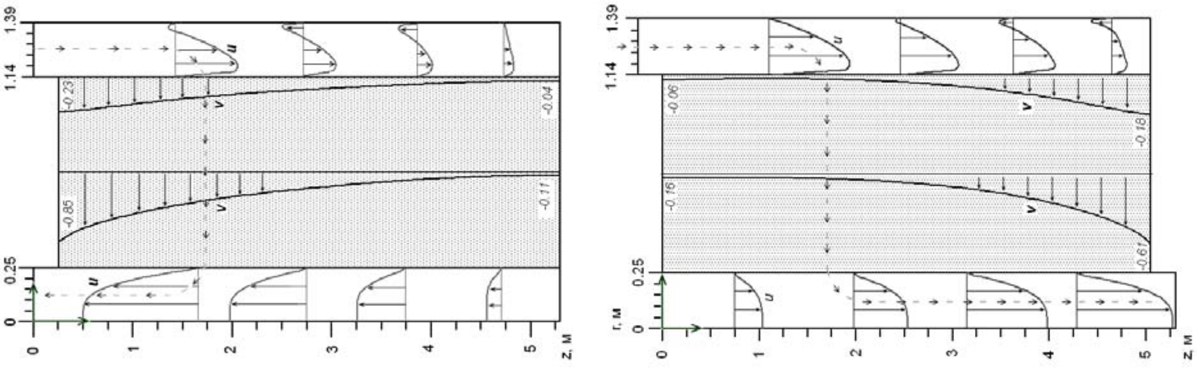
$$\left[\mu_\varepsilon\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}\right)\right]_-=\left[\mu_\varepsilon\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}\right)\right]_+ \qquad (4)$$

$$(\varepsilon v_n)_-=(\varepsilon v_n)_+,\quad (v_\tau)_-=(v_\tau)_+ \qquad (5)$$

Where: n, τ – are directions of the normal and the tangent at the interface, respectively, and indices "–", "+" refer to flow parameters before and after interface surface, respectively.

Computational solution of equations system (1) and (2) is developed meeting conjugation conditions (3) – (5) at the interfaces.

In radial flow reforming reactor crude gas flow is inputted in the line from the periphery towards to the center. Calculation data on flow dynamics at E–shaped (Fig. 1,a) and Z–shaped (Fig. 1,b) crude gas mixture inflow and outflow are given in Fig. 1.



a) b)

Figure 1 – Distribution of crude gas flow velocity in collectors and catalyst bed at E – shaped (a) and Z – shaped (b) inflow and outflow schemes in radial flow reforming reactor

At E – shaped scheme flow deceleration and mass efflux induce occurrence of extensive recirculation area in inflow collector where bulk mass of crude gas mixture cross-flows within initial domain of catalyst bed (Fig. 1,a). At Z – shaped scheme cross-flow of bulk crude gas mass occurs in the end portion of catalyst bed (Fig. 1,b). Hydrodynamic non-uniformity of crude gas flow velocity is amplified due to shortening of radius (Fig. 1).

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OP-I-15

NUMERICAL INVESTIGATION ON THE CHEMICAL GAS MIXING THROUGH INTERACTION BETWEEN JETS AND A CROSSFLOW

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An efficient combustion requires a better understanding of the gas mixing mechanisms, because a poor mixing process between fuel and oxidizer gas may generate additional formation of NO_x, for example. Besides, in the field of chemical engineering processes, the synthesis of numerous organic compounds like nitric acid, maleic anhydride or hydrogen cyanide requires a strong turbulent mixing between the reactive gases, injected upstream from the catalytic reactor. Jets exiting into a crossflow create complex and challenging three dimensional turbulent flow conditions. Mixers of such type offer some advantages in terms of efficiency, installation, cost and maintenance, and thus are widely employed.

Up to now, a single jet exiting into crossflow (JICF) has been the best investigated mixing phenomenon. However, it is noteworthy that interactions between the adjacent jets in a row cannot be predictable from a single jet [1]. Therefore, it appears important to analyse the most dominant Counter-rotating Vortex Pair (CVP) produced by twin jets exiting side-by-side into a crossflow (TJICF), as illustrated in Figure 1 with the attached coordinates system.

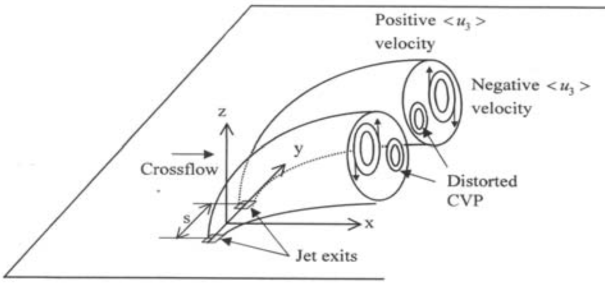
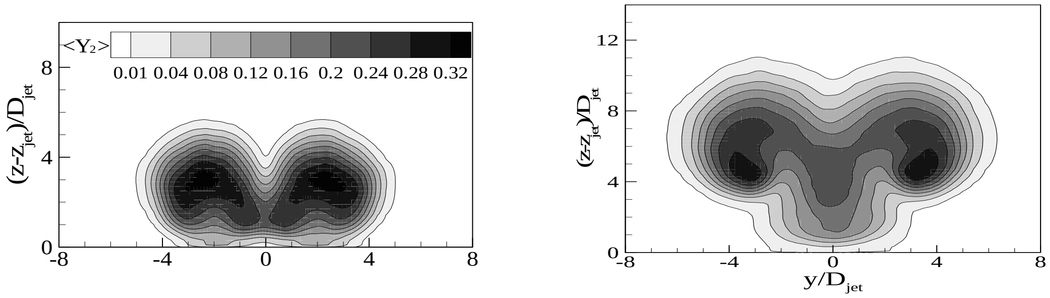


Figure 1. Twin jets into a crossflow

Savory and Toy [2] studied the influence of *S* and *r* parameters on the development of the TJICF and their remarks are the following: (i) the inner vortices rapidly diminish such that the outer vortices then form a pair similar to that of a simple jet case, (ii) both the *r* and x/D_{jet} parameters can be used as scaling and, (iii) depending on the *S* value, the crossflow passes between the jets or does not. Moreover, Vranos et al. [3] attribute the displacement towards the wall of the vortices in an opposite rotation, to the interaction with the neighbouring vortices from adjacent jets.

The aim of the present work is to further understand, by means of numerical simulation, the interactions between two jets mounted side-by-side, exiting into a crossflow in the similar conditions to those used frequently in industrial mixers. For the jet to crossflow, the primary momentum transport is sustained by large-scale energy-containing eddies, which can be completely described in a resolved scale. The resolved values are computed on a numerical grid, while the unresolved field has to be modelled by using Smagorinsky subgrid-scale model. Upon encountering the perturbation induced by the jet, the boundary layer probably changes rapidly from transition into a fully turbulent one. The computation of the turbulent boundary layer requires a high number of mesh points to describe the viscous sublayer where viscous effects are dominant, making it difficult to apply to these TJICF. The present work does not deal with predictions of local heat and mass transfer in the vicinity of solid boundaries which are critically dependent on the near-wall model due to important viscous effects. The computational nodes immediately adjacent to a solid wall are located in the fully turbulent region and this simplicity allows faster computations and by this, a higher spatial discretization and an increase of the resolved part of the spectrum. Predictions of the most dominant CVP away from the wall are generally less sensitive to the near-wall turbulence model used.

Jet velocity trajectory, as well as velocity, vorticity and, especially, mass fraction distribution are analysed in function of the blowing ratio, dimensionless distance between jet axes, and dimensionless length from the injectors. Each jet diffuses near its injector without interferences, but the interactions downstream modify strongly the shape of the distributions compared with a JICF. The mixing region is enhanced by enlarging the spacing and reaches a maximum at r=4.5-5.5 depending on the height of the mixer. Beyond this critical value, the mixing rate does not decrease in contrast to a situation with narrow spacing between jet axes. A characteristic length of merging between the neighbouring jets for high values of the parameter *S,* decreases with *r*. Besides, the Reynolds number at the injection and the shape of the injector have a little influence for intermediate *r* ratios. At last, the density ratio between jets and crossflow can affect the mixing. The role of the CVP for the dilution of the chemical gases (mass fraction) became reinforced with the blowing ratio, r, as a function the ratio, S, as evidenced in Figure 2.



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DRAG FACTOR FOR A FIXED BED AS A FUNCTION OF THE Re NUMBER WITH COMMON EXPONENT

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There are a lot of various universal expressions for the dependence of the drag factor for the fixed granular bed on the Re number of gas phase stream [1]. However, it was shown recently [2] that measured drug factor values for complex catalyst shapes, such as regular granules with more than one channel, cannot be calculated using those universal expressions.

Nevertheless, it turns [2] that data for a drag factor *vs.* Re number dependence can be successfully treated using power law like that introduced by Zhavoronkov [1]: drag factor $f_e = A\mathrm{Re}_e^{-n}$, $\mathrm{Re}_e = 4u/a\nu$, where u is the superficial gas velocity, m/s; a is the specific bed surface area, m^2/m^3; ν – the kinematic viscosity, m^2/s. A and n represent an individual set of parameters for specific type of granules.

Average deviations from a resulting curve [3] lie within the limits of 1% – 2%. Values of n so obtained vary from 0.15 to 0.29 for the catalysts examined with the standard deviation values within the limits of 0.01 - 0.03. As for A values, following groups of catalysts can be distinguished:

a) curved cylindrical extrudates of irregular length and faces, A=7.5;

b) spheres with channels, 10 mm in diameter, and solid spheres, A about 1;

c) cylindrical tablets, rings and granules of regular shapes with 7 parallel cylindrical channels, A about 2.6. Standard deviation values vary from 10% to 27%.

As the exponent n values for most of the catalyst shapes involved are close, one can try to find such a single exponent value that can be used for every catalyst, factor A values being individual at the same time. This problem was solved by minimizing the total sum of squared deviations from a regression curve taken through the whole set of catalyst types involved. Factor A values were calculated using individual sets of data for specific shapes and the common exponent value found as described. Standard deviations for the evaluated parameters were obtained using the common procedure for linear regression [3].

As a result, the common exponent n value obtained is 0.234 ± 0.007. The makeup of most groups mentioned above changed. Now one can clearly distinguish four groups of catalysts:

a) curved cylindrical extrudates of irregular length and faces, A=7;

b) cylindrical tablets and rings, A about 2.9;

c) granules of regular shapes with 7 parallel cylindrical channels, A about 2.6;

d) solid spheres, A=1.6. Standard deviation values vary from 10% to 35%.

It should be mentioned that the makeup of most groups in the case of the common exponent n value is more uniform as for the catalyst shape type. This fact additionally justifies such an approach.

Therefore, drag factor *vs.* Re number dependencies derived from data obtained as it is made in [2] are more various than it is frequently accepted.

For example, three catalyst types with bed porosity value of 0.36 have quite different A values. So even those universal expressions which take into account bed porosity are not adequate enough.

Theoretical basis of A values prediction for some definite granule shape group is the subject of further study.

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INTEGRATED BI-MODAL FLUIDIZED BED REACTOR FOR BUTANE DEHYDROGENATION TO CORRESPONDING BUTENES

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The direct butane dehydrogenation to corresponding butenes (1-butane and/or iso-butene) is the most economical route. The reaction is complex as reaction engineering constraints are very much tide up with engineering constraints due to high endothermic requirements, equilibrium limitations and reaction stereo-chemistry. The state-of-the-art idea of *bi-model particle* Gas-Solid-Solid fluidization (GSS-FBR) system was introduced in order to overcome light alkane dehydrogenation reaction barriers (i.e. continuous heat input for endothermic reaction) in a fluidized bed technology. In this study, both n-butane and iso-butane dehydrogenation reactions were studied in an integrated fluidized bed reactor (see figure 1), using Pt-Sn/Al_2O_3-SAPO-34 novel catalyst at 585°C. The results of integrated bi-model particle fluidized bed reactor were compared with fixed bed micro-reactor, and parametrically characterized. The results showed that the higher butene's selectivity above 85-92 %, with feed conversion between 30-40 % was obtained for longer reaction time up to 12 hr in GSS-FBR. This significant enhancement is achieved for continuous longer reaction duration by using novel bi-model particle fluidization system, owing to uniform heat transfer throughout the reactor and transfer of coke from principal catalyst to secondary catalyst, which increases principal catalyst's stability. The secondary catalyst, i.e. heat carrier and serve as a catalyst in secondary reactor for olefin inter-conversion reaction and/or cracking. Experimental investigation reveals that the novel Pt-Sn/Al_2O_3-SAPO-34 catalyst and proposed intensified design of fluidized bed reactor is a promising commercialization opportunity for light alkane (in particular propane, n-butane, and iso-butane, etc.) dehydrogenation to corresponding olefins, with both economic and operational benefit.

Keywords: Co-fluidization, Pt-Sn/Al_2O_3-SAPO-34, bi-model particle system, propylene, dehydrogenation.

OP-I-17

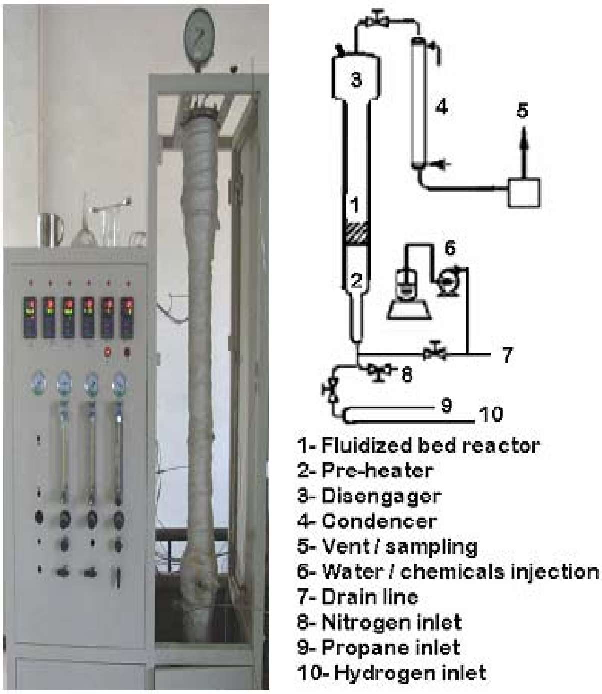

Figure 1. Hot-model of *bi-model particle* Fluidized Bed Reactor (FBR) apparatus.

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This research was conducted at FLOTU.

HONEYCOMB CATALYSTS WITH POROUS WALLS: CFD MODELING OF OXIDATION REACTION IN CHANNELS OF DIFFERENT SHAPES

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Structured catalyst systems are promising for many applications. For design purposes the data concerning the interaction of transport phenomena and reaction proceeding are desired. Simplified models do not show all features of aerodynamic processes, while CFD modeling makes available more details [1].

This study continues that of [2]. Some theoretical results are presented of transport phenomena under conditions of an exothermic catalytic reaction in a honeycomb catalyst with porous walls and triangular or square channels. The impact of the channel shape and operation conditions on the reaction rate both on the surface and in the volume of the catalyst is studied.

To obtain spatial distribution of a laminar gas flow in the honeycomb catalyst, the complete system of Navier-Stokes equations is solved by using the software FLUENT. A single channel model is used assuming the permeability of the walls for the gas flow, and the catalytic methane oxidation is under study as an example. The operation conditions were varied for the inlet temperature of 700-800°C and short contact time of 3-10 ms.

Figures 1 and 2 show an example of axial profiles of the reaction rate and CH_4 conversion averaged over the cross-section of the catalyst fragment for two cases, triangle and square channel. The geometric parameters of the catalyst fragment are such that *the hydraulic diameter of both channels is the same*, 1.18 mm; namely: channel inner side 2.044 mm (triangle) and 1.18 mm (square), open porosity 47.1 %, thickness of the monolith wall 0.54 mm, catalyst fragment length 10 mm. Inlet conditions: superficial gas velocity 2.91 m/s, methane concentration 0.83 wt.%, temperature 400°C.

Thus, the results of CFD modeling show that the performance of exothermic catalytic reactions in the structured catalyst with porous walls and channels of different shapes is characterized by significant in homogeneity of the gas flow, temperature, and reaction rate in the catalyst volume. Maximum reaction rate near the inlet is higher comparing to an impermeable monolith due to the gas flow penetration through the catalyst frontal surface.

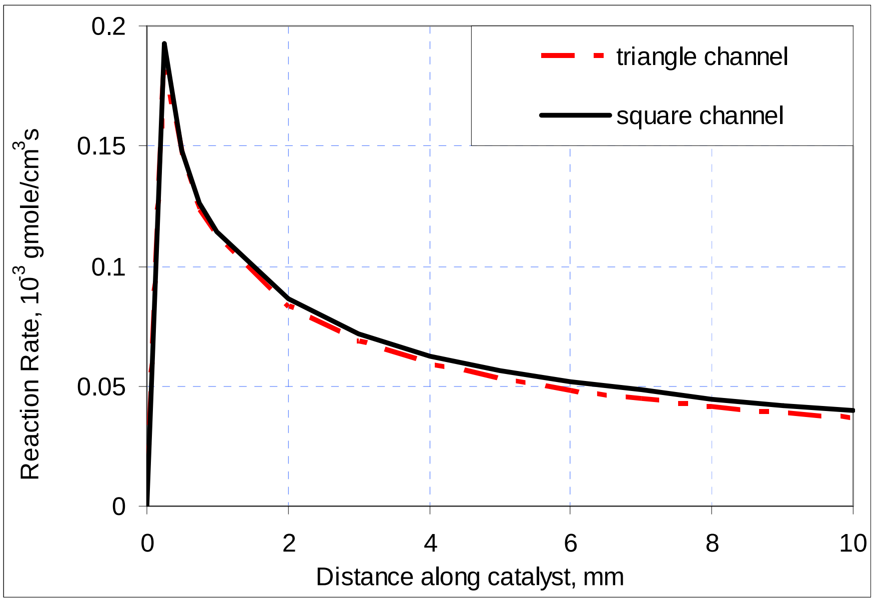

Fig. 1. Axial profiles of the reaction rate averaged over cross-section

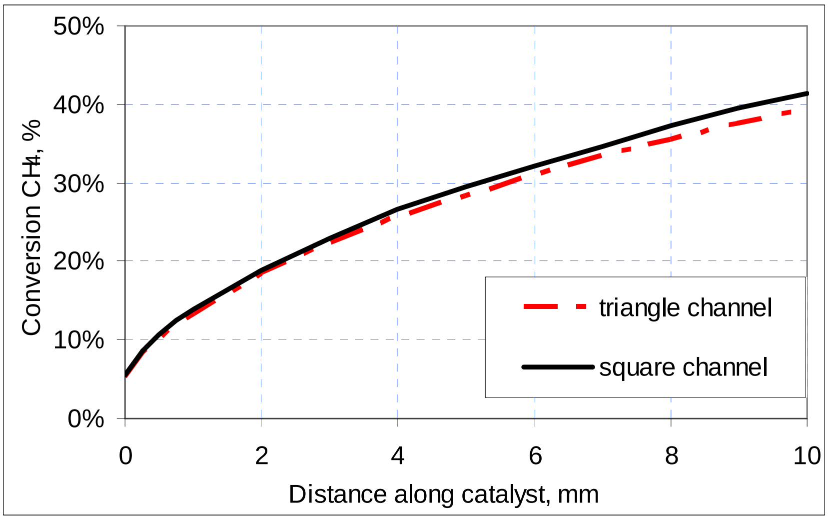

Fig. 2. Axial profiles of methane conversion averaged over cross-section

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Acknowledgements

Support by SB RAS Interdisciplinary Integration Project no. 80 is gratefully acknowledged.

OP-I-19

A MULTITUBULAR REACTOR SYSTEM FOR PARALLEL SCREENING OF CATALYSTS FOR RING OPENING OF DECALIN IN CONTINUOUS MODE

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Introduction

Ring opening of decalin (Figure 1) is an important reaction for synthesis of diesel type fuels, which attracted a lot of attention recently with research being mainly focused on mechanistic aspects. Only few reports are available when this reaction was investigated in a continuous mode. A continuous reactor was applied in order to emphasize especially the long-term activity and catalyst deactivation over three different catalysts, namely Pt/Beta, Pt/Ir-Beta/alumina and Pt/Ir-Beta/silica. The taylor-made reactor system gives a possibility to use two or three phases, realistic catalyst particle sizes, provides a possibility to perform parallel screening of various catalysts as well as to study temperature effects, recognising catalyst deactivation and allowing transient and steady state operations.

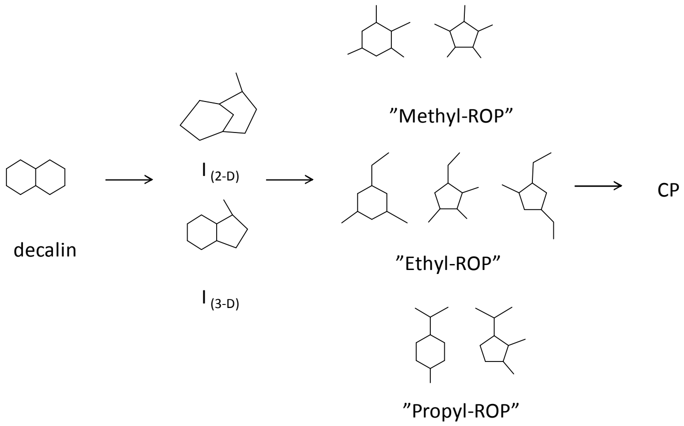

Fig. 1. Reaction scheme for ring opening of decalin, notation I=isomer, ROP, ring opening products, CP= cracking products.

Reactor Setup and Operation

A reactor system consisting of six parallel tube reactors (d_i = 10 mm) was constructed in house (Figure 2a). Gas flows were controlled with four mass flow controllers and pressure with the help of backpressure controllers. The temperature of each reactor was controlled separately. Liquid samples were withdrawn from the outlet of each reactor and analysed by GC. The catalytic activity of 0.5 wt% Pt/Beta, 0.4 wt% Pt-1.2 wt% Ir-Beta/alumina, and 0.4 wt% Pt/ 1.4 wt% Ir-Beta/silica was evaluated for ring opening of decalin. Typically 1.6 g of the catalyst, 150-350 µm, was packed in the reactor in a way that the volume of the catalytic bed was equal in each reactor and corresponded to WHSV = 10 h^{-1}. In addition, WHSV of 5 and 20 h^{-1} were applied. The catalysts were reduced prior to the experiments *in situ* for 3 hours at 350 °C at ambient pressure. When the desired temperature was reached, the experiment was started applying a liquid feed rate of 0.6 ml/min and the hydrogen gas flow rate of 100 ml/min through each reactor under 4 MPa H_2. The catalysts were characterized by nitrogen adsorption, pyridine adsorption desorption with FTIR and CO pulse chemisorption. Furthermore, coke in the spent catalyst was investigated.

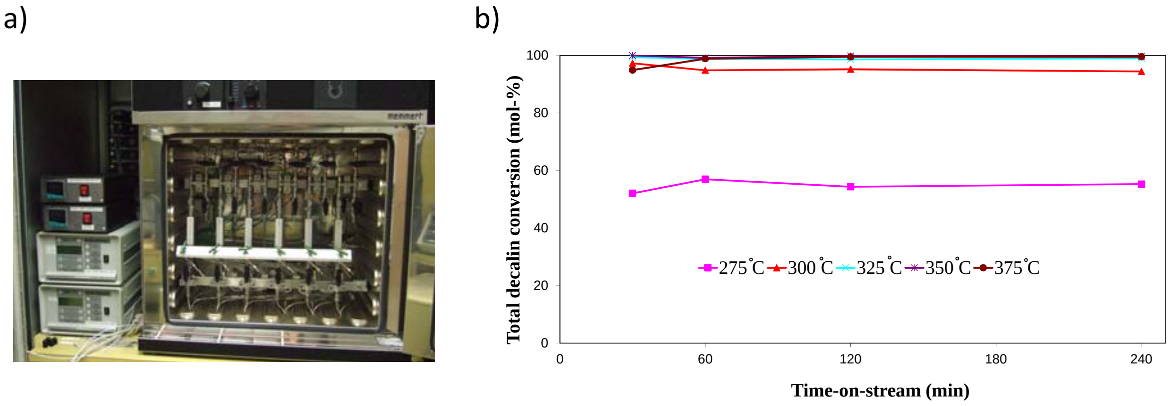

Figure 2. A photograph from the parallel reactor system and b) conversion of decalin at different temperatures over Pt-Beta.

Results

The results from activity tests were correlated to the catalyst acidities and surface area changes. In addition, the experimental results indicated that under optimized (300 °C, 4 MPa H_2) conditions none of the tested catalysts was severely deactivated with time on stream. However, when the temperature was increased to 325 °C carbon deposition over all the tested catalyst started to be predominant (Figure 2b). The highest selectivity to ring opening products was achieved at 300°C being 30% at 94% conversion.

Conclusions

Continuous reactor system was demonstrated to be an efficient tool for investigating catalyst activity and stability in ring opening of decalin facilitating rapid screening of different catalysts and reaction conditions.

3D SWIRL FLOW REACTOR TECHNOLOGY FOR PYROLYSIS PROCESSES: HYDRODYNAMIC AND COMPUTATIONAL FLUID DYNAMIC STUDY

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Pyrolysis is the main process for the production of almost all valuable organic base chemicals, especially ethylene and propylene. Traditionally tubular reactors suspended in large gas fired furnaces are adopted. The gas phase reactions are accompanied by secondary reactions leading to the formation of coke on the inner walls of the reactor tubes [1]. This carbonaceous coke layer leads to an increased pressure drop over the reactor and a lower heat transfer rate, resulting in a higher tube metal temperature to maintain the same conversion. The decrease in olefin selectivity due to a higher pressure drop and the higher energy consumption due to coke formation have a detrimental effect on the cracker's economics [2]. Moreover carburization can lead to deterioration and/or damage to the tube material [3]. Hence ethylene producers and engineering contractors have and continue to be interested in new technologies to reduce coke formation. The latter can be divided in three categories: the use of additives and coatings, development of new reactor alloys and new reactor designs.

This work investigates a new development in the last category, i.e. Technip's patented Swirl Flow Tube (SFT) [4]. An example of a Swirl Flow Tube is shown in Figure 1. Whereas typical steam cracking reactors are tubular reactors with a straight centerline, the current reactor has a centerline with a helical path with the amplitude less than the inner radius of the tube. When fluid enters this type of piping, swirl flow is established almost immediately. Furthermore, the secondary motion and mixing over the cross section associated with the swirl flow results in enhanced mass, momentum and heat transfer [4].

Figure 1: Example of Technip's patented Swirl Flow Tube.

The current contribution will discuss on the one hand an experimental study of pressure drop and heat transfer experiments with air. Three tubes (1 conventional tubular reactor and 2 SFT designs) were tested for a Reynolds range of 20000 to 120000.

On the other hand, the contribution will discuss the results of a study of the hydrodynamics of the SFT using the commercial package Fluent 13.0. The model results were validated by comparison with experimentally measured friction factors and overall heat transfer coefficients. Good agreement was obtained (avg. rel. error <5%) by adopting the Reynolds-Stress-Model and properly resolving the near wall region with a two layer model. The enhanced heat transfer is attributed to the swirl flow scouring the tube walls. Furthermore Dean vortices develop enhancing the mixing from the boundary layer to the tube core.

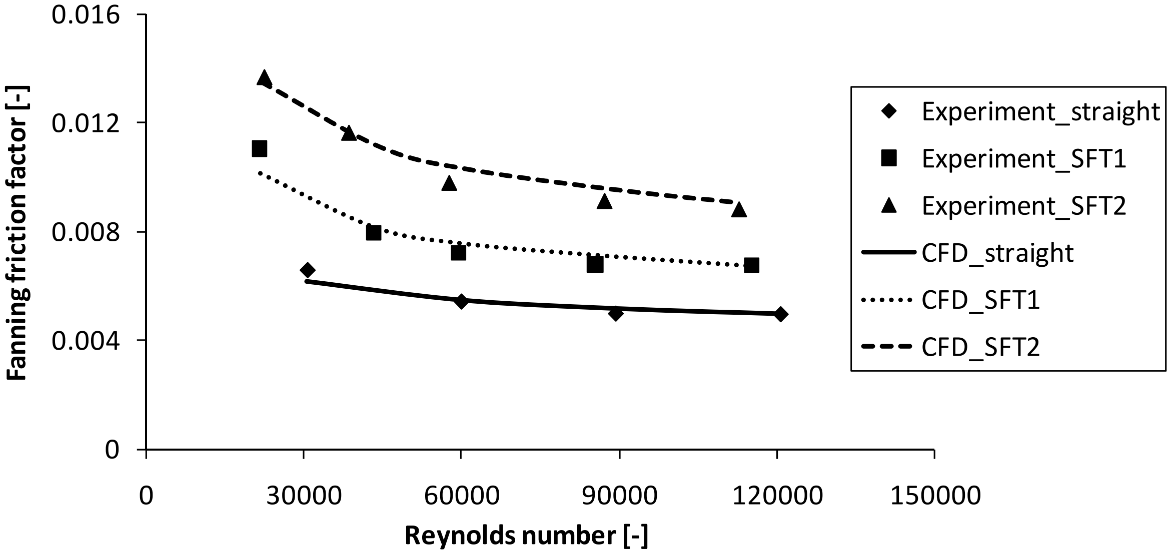

Figure 2: Experimentally measured and simulated Fanning friction factors.

After validation of the model, a parametrical study was performed to study the effect of geometrical parameters on pressure drop, mixing and heat transfer. The two geometrical degrees of freedom are the helix relative amplitude and relative pitch. Optimal values for different Reynolds numbers are presented, allowing the proper design of SFTs for industrial applications. The results confirm the high potential of swirl flow tube reactors for reduced coke formation during light olefin production.

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OXIDATIVE CONVERSION OF LIGHT ALKANES

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Introduction

Effective production, transportation and processing of various resources of gaseous hydrocarbons including those from untraditional and low debit sources such as associated oil gas, coalbead methane, shale gas, tight gas and others becomes one of the most important industrial problems. Gas industry needs a variety of new more simple, flexible and mobile low-scale technologies for gas conversion just at places of its production into more valuable and easily transportable products. Oxidative conversion of light alkanes into olefins and oxygenates is one of the most prospective approaches to solve this problem. There are a lot of studies on oxidative conversion of methane [1,2]. Significantly lesser number of works is dealing with its homologues [3]. Depending on the process pressure, temperature and other parameters oxidative conversion let to obtain such valuable products as olefins, alcohols, aldehydes and others. Recently new process of selective oxidative conversion of C_3+ admixtures in raw natural and associated oil gases, mostly to ethylene and hydrogen, was developed that let to use effluent gas as a fuel for gas piston and turbine power engines [4,5]. In this paper are presented some related results on partial oxidation of low admixtures of ethane and propane to methane or inert gases (N_2 and He) at atmospheric and enhanced pressures.

Experimental part

All experiments were performed at flow conditions in quartz (at atmospheric pressure) or stainless steel lined with quartz (at enhanced pressures) externally heated reactors with inner diameters 14 mm and 7 mm, correspondingly. The uniformly heated length of both reactors was about 200 mm with reaction time in both cases in a range of several seconds. More thorough description of high pressure installation is given elsewhere [6]. Experiments on conversion of ethane were accompanied by kinetic modeling using our model (more than 400 elementary stages) for partial oxidation of C_1-C_2 hydrocarbons at elevated pressures (1-100 atm) and enhanced temperatures (300-1000°C).

Results

Oxidative cracking of ethane at atmospheric pressure shows noticeable gas phase conversion of reagents only at $T > 650°C$. At dilution by N_2 and He sharp transition to complete oxygen consumption evidences the chain-branched character of the process (fig.

1). On the contrary, in methane the process proceeds with a steady increase of conversion. The increase of conversion at low temperatures can be interpreted as a promotion of propane oxidation by methane, probably due to very fast chain-branching at oxidation of methane, similar to that observed at enhanced pressures [1,2]. At lower temperatures main primary products are ethylene and water, but with temperature and time their selectivity decreases in favor of H_2, CO and CH_4. At short (<1 s) time the interaction between ethane and oxygen takes place at the whole length of reactor, but temperatures of full conversion for ethane are noticeably higher than that for oxygen. Kinetic simulation describes well these results.

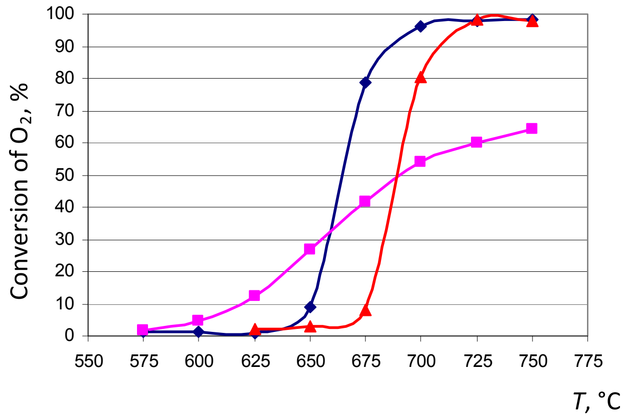

Fig. 1. Oxygen conversion vs. temperature at oxidative cracking of ethane in He (▲), N_2 (♦) and CH_4 (■). $[C_2H_6]$ = 5%, $[O_2]$ = 2,5%, t_r = 2 s.

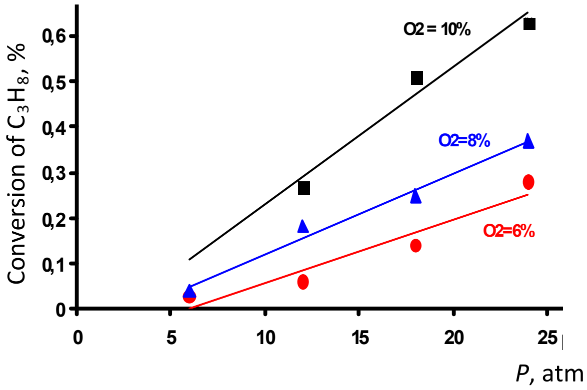

Fig. 2. Propane ($[C_3H_8]_0$ = 14 - 29%) conversion in methane vs. pressure at $[O_2]_0$ = 6% (●), $[O_2]_0$ = 8% (▲) and $[O_2]_0$ = 10% (■). T = 520-550°C, t_r = 1,8 s.

Conversion of propane accelerates at the increase of pressure and oxygen concentration (fig. 2) with evident negative methane conversion (methane production as a result of propane decay). But there seems the existence of the threshold of reaction at pressures below ~5 atm. We also observed an evident temperature hysteresis in this reaction with temperature of reaction quenching being about fifty degrease lower than temperature of its beginning.

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ORAL PRESENTATIONS

SECTION II

Chemical Reaction Engineering and Reactors Design – Novel Approaches, Modeling, Scale-Up, Optimization

New Designs of Chemical Reactors (Membrane Reactors, Microreactors, Structured Reactors, etc)

Novel Approaches in Chemical Reaction Processes Engineering (Unsteady-state and Transient Processes, Reverse-flow Operation, Sorption-Enhanced Reaction Processes, Multifunctional Reactors, Reaction-Separation Processes, etc)

OP-II-1

CATALYTIC OR THERMAL REVERSED FLOW COMBUSTION OF COAL MINE VENTILATION AIR METHANE: WHAT IS BETTER CHOICE AND WHEN?

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Keywords: Reversed flow reactors, catalytic combustion, thermal combustion, methane, VAM.

Introduction

Problem of the coal mine shafts ventilation air methane (VAM) utilization as widely known will be only briefly presented in the paper. The most attractive way of this utilization seems to be combustion in the flow reversal reactors (FRRs), namely: either catalytic - CFRRs or thermal (also been called the homogeneous) - TFRRs. Su et al [1] presents and compares both methods. Good discussion of the two types, but from the point of view of volatile organic compounds (VOC) combustion economical feasibility, was given by Matros et. al in [2] (where FRRs was been called as regenerative oxidizers either catalytic - RCO or thermal – RTO). The problem of VAM mitigation is different, however, mainly because in some cases large amount of heat can be recovered. Thus economy and technical demands of the heat utilization should also be taken into account. Concentration of VAM varies significantly and it depends on particular coal mine (for USA see e.g. [3]). Usually this concentration is below 1 vol.%, but there are some of them [3], where even average value exceeds 1 vol.%. On the other hand there are many mines where average concentration is about 0.3 vol.% or sometimes even lower. There could be two goals for the VAM utilization, either environmental mitigation of this strongly greenhouse gas (GHG) emission or energy recovery, or both. The paper will analyze how these two goals affect the technical solutions.

FRRs for greenhouse gas mitigation, for heat recovery or both goals?

Methane as the GHG has a global warming potential (GWP) at least over 20 times higher than CO_2. Therefore combustion even without the heat recovery could be ecologically or economically attractive. Matros & Bunimovich in [4] claim that CFRR (RCO) requires adiabatic temperature rise ΔT_{ad} > about 15 °C to be autothermal, while the similar threshold for TFRR (RTO) is 50 – 90 °C. This means that VAM combustion CFRR could be autothermal for CH_4 concentrations above ~ 0.06 vol.% while TFRR requires at least ~ 0.19 vol.%, what generally agrees with conclusions given in [1]. Thus advantage of CFRR over TFRR for very low concentrations seems to be obvious. On the other hand when significant heat recovery is taken into account, i.e. for concentrations above 0.5 vol.% lit. [5] revealed, that CFRR maximum temperature is too high to use any cheaper catalyst. For concentrations close to 1 vol.% even if Pd catalyst is used then its temperature can increase over the permissible limit.

Sometimes temperature in TFRR higher of about 300 ^{o}C over the temperature in CFRR is considered as its drawback. Experiments carried out on a TFRR research & demonstration plant [6] revealed that a maximum temperature reached 1100 ^{o}C for CH_4 1 vol.% at the reactor inlet. Due to the flameless combustion in monolith reactor even traces of NO_x did not appear, however. A discussion of influence of the reactor temperature on the amount of heat recovered reveals that the higher temperature the higher heat recovery is. Moreover, low-temperature heat carrier makes it difficult or even unfeasible production of valuable form of energy (high pressure steam or electricity). The paper discusses the heat recovery options from the technical point of view, illustrated by simulated and experimental results taken from the TFRR plant.

Summarizing: When VAM concentration is low (approx. below 0.4 vol.%) CFRR could be an appropriate solution for greenhouse gas mitigation, but the heat recovery (if any possible?) would generate low grade heat carrier difficult to be utilized at the coal mine, since demand for such heat in these circumstances is low. However, generally one might conclude that the TFRR is more advantageous than CFRR when high grade heat recovery is expected.

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OP-II-2

REVERSE-FLOW REACTOR CONCEPT FOR COMBINED SO_2 AND CO OXIDATION IN SMELTER OFF-GASES

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SO_2 abatement in waste gases of non-ferrous smelters is an important environmental protection problem. The most effective technology for solution of this problem is the catalytic SO_2 oxidation reverse-process [1], but its efficiency decreases under presence of CO in smelter off-gases gases (the application of novel smelter technologies in non-ferrous metallurgy leads to this complication). CO oxidation is strongly exothermic and it occurs at conventional vanadia catalyst in the SO_2 oxidation reactor at rather high temperatures (above 500°C) thus leading to overheating of catalyst beds resulting, in turn, in corresponding decrease of equilibrium SO_2 conversion. Therefore, the development of the effective CO oxidation catalyst, capable to work stably in SO_2 environment and at lower temperatures, is actual. The problem may be resolved by application of the platinum catalyst on the glass-fiber support [2], which may effectively oxidize both CO [3] and SO_2 [4], demonstrating high operation stability in the conditions of real sulfuric acid manufactures [5].

Experiments were carried out with 0.02% Pt catalyst on Zr-Si glass-fiber support (GFC), with a mixture modeling the composition of the metallurgical waste gases.

To model the long-term SO_2 deactivation influence we used the catalyst preliminary treated for more than 1000 hours in real gases of industrial SO_2 oxidation process [5].

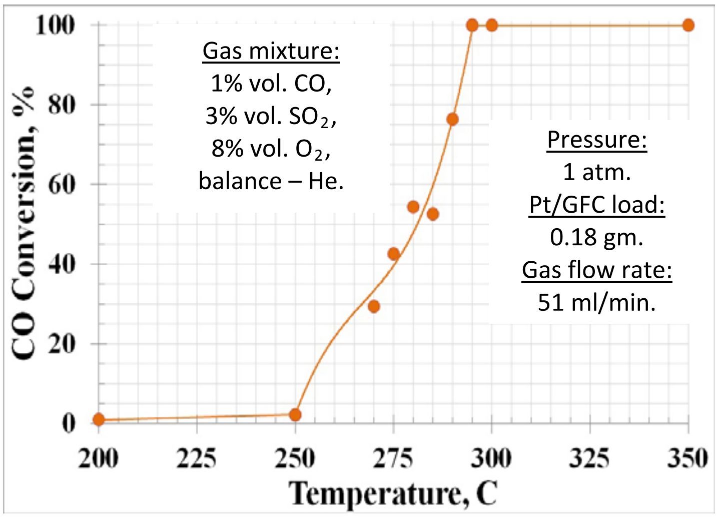

Fig. 1. CO conversion vs. reactor temperature.

It was shown (fig. 1) that the Pt/Zr-Si-GFC is capable to provide complete CO conversion in SO_2 presence at temperatures less 300°C, at the same time showing high resistance to deactivation.

Pt/Zr-Si-GFC beds may be optimally placed in the reverse-flow reactor between beds of inert heat-regenerative packing and vanadia catalyst (fig. 2).

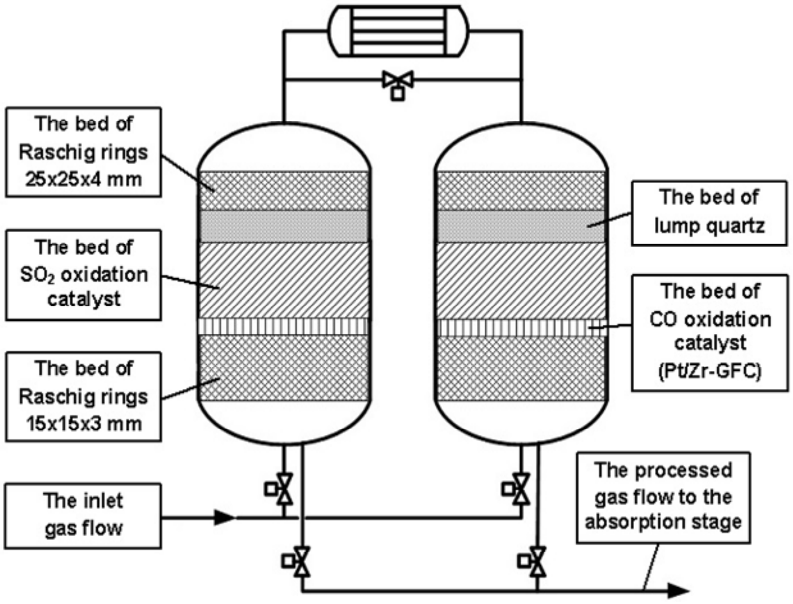

Fig. 2. Flow-sheet of the reverse-flow SO_2 oxidation reactor with additional beds of Pt-GFC for CO oxidation.

The performed mathematical simulation showed that introduction of additional Pt/Zr-Si glass-fiber catalyst beds for CO oxidation in the reverse-process of SO_2 oxidation allows to essentially lower the maximum temperature in the catalyst beds by separate low-temperature CO oxidation, which heat doesn't essentially influence the maximum temperature in the beds of vanadia catalyst for SO_2 oxidation, and thus to increase the equilibrium SO_2 conversion and improve the overall process stability under CO content oscillations.

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MODELLING OF A CONTINUOUS ROTARY REACTOR FOR CARBON NANOTUBE SYNTHESIS BY CATALYTIC CHEMICAL VAPOUR DEPOSITION

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The modelling of carbon nanotube production by the CCVD process in a continuous rotary reactor with mobile bed was performed according to a rigorous chemical reaction engineering approach. The four factors governing the reactor are geometric, hydrodynamic, physical and physico-chemical factors. They were analyzed separately in order to establish the reactor equations. Concerning geometric and hydrodynamic factors, it was demonstrated that both gas and solid flows can be represented as co-current plug flows in the tubular inclined reactor. Concerning the physico-chemical factor, the initial true reaction rate equation had been previously determined and a catalytic deactivation study was performed in a discontinuous reactor, determining that the catalyst follows a sigmoid decreasing law during carbon nanotube growth. Finally, the study of the physical factor highlighted the fact that diffusion of ethylene occurs much faster than the chemical reaction and that ethylene diffusion though the catalytic bed is not the limiting factor. Furthermore, the heat transfers were studied and were found to be negligible.

Once the four factors governing the reactor process were known, the reactor equations could be written. So the modelling of carbon nanotube production in a continuous inclined rotary reactor was performed, applying the co-current plug-flow hypothesis and taking the true kinetic equation and the sigmoid catalytic deactivation into account. The reactor modelling allowed obtaining partial pressure, carbon nanotube production, catalytic deactivation and the temperature profiles through the reactor. The comparison between the experimental and the calculated productivity showed that the calculated data fitted very well with the experimental data, and that the modelling was in agreement with the experiments [1].

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DIAGNOSTICS AND CONTROL OF COHERENT FLOW STRUCTURES IN A PREMIXED COMBUSTOR

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The present work is dedicated to the experimental study of turbulent flow in premixed propane-air and methane-air flames by using a particle image velocimetry (PIV) technique. The analysis is aimed on role of organized large-scale flow structures on stabilization of the flames and on a potential to affect the combustion process by controlling the structures. Thus, active (periodical forcing, viz., imposing oscillations to the mixture flowrate) and passive (application of swirl) ways to control the flows were utilized during the study. For a number of studied regimes, ensembles of the instantaneous velocity and vorticity fields were measured by a stereo PIV system, and the time-averaged characteristics of velocity pulsations were calculated. The results were compared for the non-reacting and reacting flows. Besides, a high-repetition PIV system (with acquisition rate of about 1 kHz) was utilized in order to investigate dynamics of the large-scale vortices. Statistical methods allowing to extract coherent structures from velocity fields of turbulent flows were applied. For detection of turbulent combustion domain, CH* chemiluminescence signal of the flames was captured by an UV sensitive ICCD camera.

Figures 1 and 2 show the example of the periodic forcing (see details in [1]) effect on a strongly swirling propane-air lifted flame (U_0 is a bulk velocity of the mixture, d is a diameter of burner). Figure 1, depicting radiation of the flame, demonstrates a decrease of the soot in the diffusion region of the flame when the forcing was applied. CH* chemiluminescence signal reveals that this effect was accompanied with an local increase of combustion rate in the region of turbulent premixed combustion. Figure 2 shows phase-resolved structure of the most powerful vortex structures from the measured PIV data. The processing vortex core with a secondary helix in the outer mixing layer dominated dynamics of the unforced flow and process of the mixing before the flame base. When the strong forcing was applied, ring vortices were formed in the mixing layer and a weakening of the core precession took place. The ring vortices also resulted in a greater mixing of the fuel and ambient air.

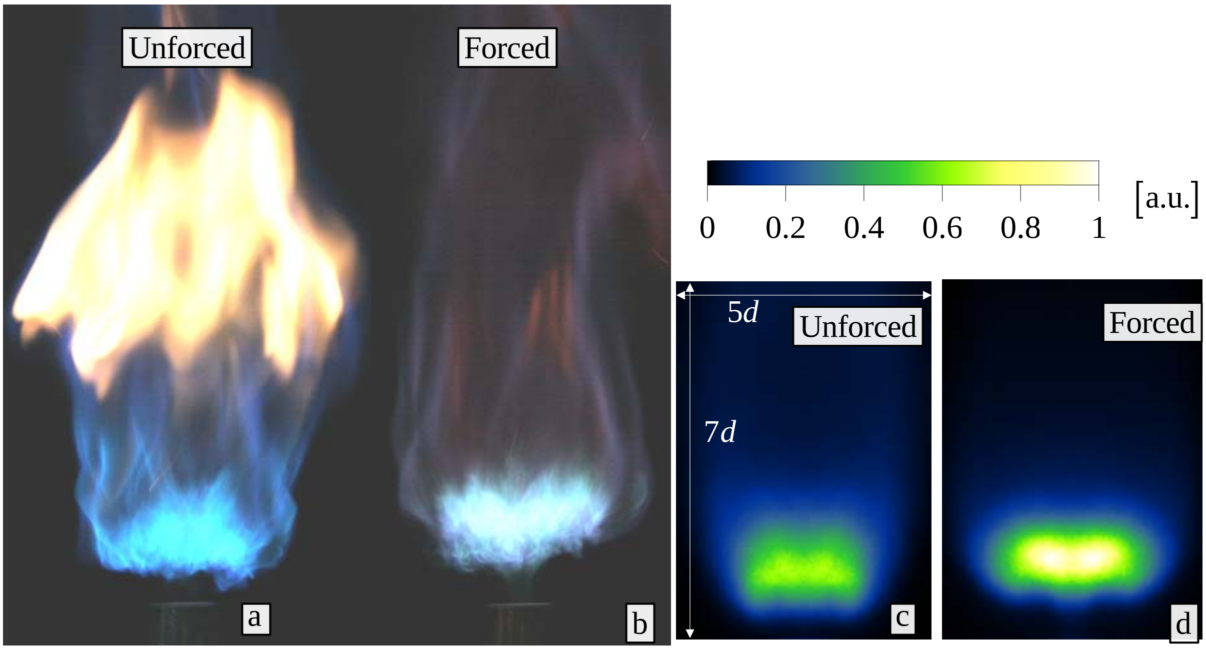

Figure 1. (a, b) Direct images and (c, d) CH* chemiluminescence of a lifted strongly swirling propane-air flame, (a, c) Unforced and (b, d) forced flow.

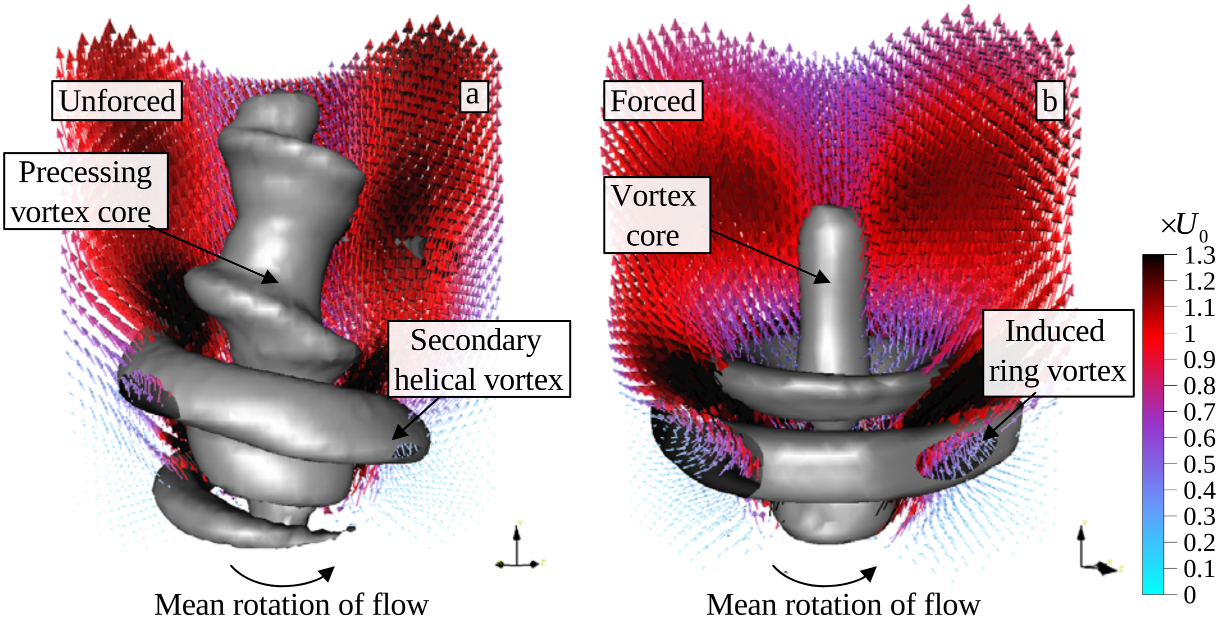

Figure 2. Phase-locked reconstruction of the most powerful vortex structures in a lifted strongly swirling propane-air flame. (a) Unforced and (b) forced flow

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OP-II-5

PHOTOVOLTAIC SOLAR ELECTRO-OXIDATION REACTOR (PSEOR): ENERGY BALANCE

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Advanced Oxidation Processes (AOPs) are the forefront technological options to remove pollutants from waste water streams. Within AOPs, electro-oxidation (EO) technology shows interesting advantages such as modularity, easy control and automation, no need of chemical reagents and no sludge generation. Some recent publications have shown a wide treatment versatility considering its capability to treat even relatively low organic matter from textile effluents [1], reverse osmosis concentrates [2], high-salinity industrial waste water [3] and aquaculture saline water [4] among others. However, the main handicap of the EO does rely on the electric energy consumption per unit of volume treated. Consequently, in order to avoid pollutant transfer between environmental compartments (in this particular case from water to air), it becomes clear that the integration of renewable primary energy is an eco-innovative approach to overcome the CO_2 emissions associated with the electric consumption. The intensification of the EO process by means of the direct use of photovoltaic solar energy constitutes a novel trend because it promotes a change in the energy source and consequently an environmental friendly profile as the demand of primary energy process comes from a renewable source [5].

The aim of this work is the analysis of energy balance corresponding to a Photovoltaic Solar Electro-Oxidation Reactor (PSEOR), in which the reactor (whose electrodes are made of Boron-Doped Diamond) is directly powered by a set of Photovoltaic Solar modules in order to remove Chemical Oxygen Demand from glucose based synthetic solutions in a transient operation mode. Figure 1 shows the main items of lab scale plant. The energy balance for the PSEOR should consider two different

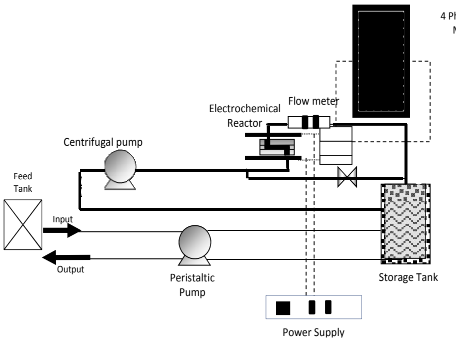

Figure 1. Set up of the lab scale plant

relationships. Firstly, the transformation of solar irradiation (*G*) in to electrical current (*I*): preliminary obtained data confirms previous works [5] in which a linear relation between solar irradiation and applied current is advised. Secondly, the relationship between the applied current density *i* and the applied voltage *U* as becomes $U=a+b*\log(i)+c*i$ *(eq. 1)* where a, b and c are adjusting parameters, being *c* related to effluent conductivity and electric internal resistances. Consequently, the relationship between *U* and *G* is similar to that presented in eq. 1 and the stochastic change of *G* has impact on *U* in a similar way, thus the treatment corresponds to a transient operation mode necessarily. Under a minimum *G*, *U* becomes too low to generate hydroxil radicals in the BDD anode. Values over that minimum *G* leads to organic matter removal. This operation mode is far away from the conventional EO, in which the applied pair *U-I* is almost constant. Preliminary experimental data of the PSEOR lab scale plant under this stochastical transition operation mode will be presented so the minimum *G* and *U* values of the system required to start the degradation of organic matter will be given.

The efficiency of the Spanish grid mix is around 44%, since the production of 3.6 MJ of electric energy requires 6.66 MJ and 1.55 MJ of non renewable and renewable energy respectively [6]. Under continuous operation, a typical specific energy consumption in conventional EO could be around 500 $\text{MJ}\cdot\text{m}^{-3}$ (depending on conductivity and removal efficiency), so 925 $\text{MJ}\cdot\text{m}^{-3}$ of non renewable primary energy are required. In the case of the PSEOR, the specific energy consumption value could be really high (about 3 times for similar conductivity and removal efficiency), as a worse exploitation of the available *I* takes place because of the stochastic nature of *G*. However, in the PSEOR only solar irradiation is needed to obtain the required electrical current, so 0 $\text{MJ}\cdot\text{m}^{-3}$ of non renewable energy are required for the oxidation of organic matter.

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OXIDATION OF AMMONIA TO NOx IN A TWO-BED (Pt GAUZES + OXIDE MONOLYTIC LAYER) REACTOR: EXPERIMENTAL STUDIES AND MATHEMATICAL MODELLING

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The process of ammonia oxidation to NOx by two-bed (Pt gauzes + monolithic oxide layer) technology in UKL-7 plant is widely used for last years in Russia to produce nitric acid. Earlier it was stated that the role of monolithic catalyst replacing part of gauzes consists not only in oxidation of slipped ammonia but also makes the gas flow distribution inside the gauzes pack more uniform thus resulting in lower mechanical and chemical loses of platinum [1]. While the main features of the bulk oxide monolithic catalyst production technology are widely discussed, another consequence of monolith installation is practically omitted from consideration, i.e., possible change of temperature profile along gauze pack due to screening effect. Meanwhile, this question is of great importance since last studies showed importance of secondary NH_3 – NO interactions for the formation of N_2 and N_2O [2]. Efficiency of these reactions running on 2nd and following gauzes in the pack can depend substantially on the degree and selectivity of NH_3 conversion on the frontal gauze and thus determined by its temperature as well.

Main goal of the present study was to reveal and evaluate the effect of heat transfer characteristics of structured monolith catalyst on the gauze pack performance.

Experimental. Monolith samples of different composition (cordierite and BIC-42-1) and geometry (shape and size of channel, as well as thickness of channel walls were varied) were prepared. Study of the effect of monolith composition and geometry on NOx yield after two-bed system and temperature profile along catalyst bed was carried out using a tube reactor equipped by thermocouples installed after the first and the last platinum knitted gauzes and after the monolith fragment. Operation conditions in the reactor (pressure, temperature, flow rates) corresponded to those in the industrial medium pressure AK-72 plant. To increase the validity of obtained data, in addition to real NH_3+air mixtures, measurements of all reaction products have been performed using the artificial NH_3+Ar+O_2 mixtures.

Reactor modeling. A two - phase transient one-dimensional reactor model was used for both Pt gauzes catalyst and honeycomb monolith. The mathematical model contains detailed species mass and energy balances both for gas and solid phases. The one-dimensional model is feasible because of uniformity of experimentally obtained radial temperature profiles in the reactor. In such a model both a gas and a solid phases species composition and temperature are taken as constant throughout the reactor cross section, while the temperature and concentration gradients between gas and solid phases are located near the solid phase surface. Spatially non-uniform heat and mass transfer between gas and solid phases with parameters depending on channel shape and size were used in monolith catalyst. Substantial heat transfer took place along the solid walls of the channels and depended on material of the honeycomb monolith. Heat exchange due to radiation between solid phases of Pt gauzes and honeycomb monolith was given by Stefan's law. The emissivity of materials (the relative ability of their surfaces to emit energy by radiation) was defined depending on composition of the solid phase of Pt gauzes and monolith. The following assumption was used in mathematical model: axial thermal conduction in the gas and solid phase; convective heat and mass transfer in axial direction; thermo diffusion in the gas phase; heat transfer due to different thermal capacities of diffusing species in gas phase; heat and mass transfer between gas and solid phases; volume change caused by a reaction stoichiometry and resulting in an axial convective mass flux. Physical properties of the reaction mixture were given as functions of temperature, pressure and mixture composition. Heterogeneous reactions were considered to occur mainly on Pt gauzes.

The numerical study of the two-bed reactor was compared with experimental data to show sufficient reliability of the mathematical model developed. The effect of such parameters as shape and size of channel, thickness of channel walls and monolith composition on the temperature profile in the gauze pack, NO_x yield after two-bed system was elucidated. Developed mathematical model is able to predict the behavior of two-bed system with the honeycomb monolith followed the Pt gauzes in the plant reactor.

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MATHEMATICAL MODELING OF THE MULTIDISPERSED ADSORPTION-CATALYTIC SYSTEM FOR REMOVING ORGANIC IMPURITIES FROM WASTE GASES

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Removal of volatile organic compounds (VOCs) from industrial waste gases is a very important problem of atmospheric air protection. Particularly there is an acute problem in cleaning gases with the very low VOC concentrations (below 0.1 g/m^3) as their treatment requires high energy consumption. In terms of this criterion adsorption-catalytic processes, including adsorption of VOC at the catalyst surface at ambient temperature with periodical incineration of accumulated VOC at elevated temperature [1-3] are of particular interest. But they have some disadvantages, such as possible desorption of unoxidized VOC to gas stream during regeneration [4], thus reducing purification degree. So, there is the need to develop new technological approaches aimed to minimize such desorption losses.

One of such approaches is application of the multidispersed adsorption-catalytic packing [5, 6], consisting of comparatively large pellets (2–20 mm in diameter) of the catalyst-adsorbent and of catalytically active micro-fibers with typical thickness of ~ 10 microns [7].

During the heating at the regeneration stage the micro-fiber catalyst will be heated much more rapidly than adsorbent-catalyst, due to the much higher unit outer surface area improving the heat exchange. When the adsorbent-catalyst temperature will become high enough for partial desorption of chemisorbed VOC, the temperature of the micro-fibrous catalyst will be already as high as necessary one for complete oxidation of desorbed VOCs. Such operation mode provides minimization of desorption losses to required level (Fig. 1), at the same time giving the way to keep all benefits of known adsorption-catalytic processes.

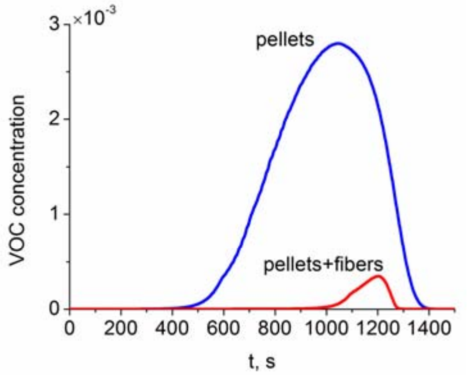

Fig. 1. VOC concentration at bed exit

This theoretical concept was confirmed by results of the mathematical simulation of combined multi-dispersed system. It was shown, that addition of the microfibrous catalyst leads to significant improvement of the purification efficiency of the adsorption-catalytic process (Fig. 2). Also calculations have shown that integral energy consumption at the regeneration stage may be reduced by switching off the inlet air heating. There exists an ignition time (vertical dashed lines in Fig. 3), after that the regeneration is passing on in self-ignition regime. It can be seen that ignition time is less in multidispersed bed, than in the bed containing no fibers. So, addition of microfibrous catalyst also allows to reduce minimal energy consumption, required for the efficient and stable process performance (Fig. 3).

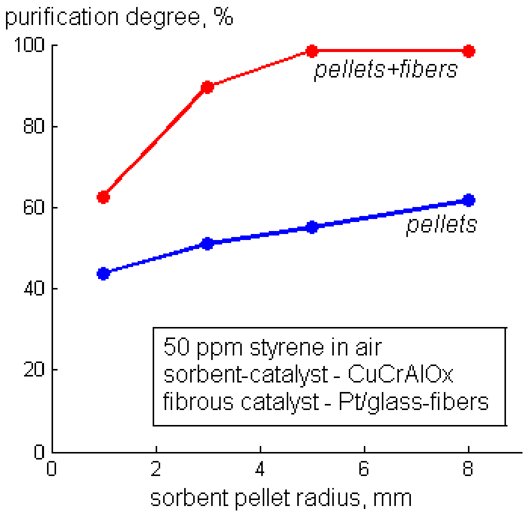

Fig. 2. Purification degree depending on pellet radius

Fig. 3 Integral energy consumption depending on hot air feeding duration

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SCALING UP HIGHLY PRODUCTIVE FISCHER-TROPSCH REACTOR FROM LABORATORY TO PILOT SIZE

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It is commonly accepted that the productivity of Fischer-Tropsch reaction is one of the keys to economic efficiency of the whole XTL process. The expression for calculation of productivity P_{FT} is shown below in equation as mass of total liquid phase products M_{liq} per volume of catalytic bed V_{bed} in period of time t:

$$P_{FT} = \frac{M_{liq}}{V_{bed} \times t} \quad .$$

Although there are many other types of productivity definition in literature, the one shown in equation is the best for understanding relation between catalyst properties and reactor performance parameters. The productivity is closely related with the catalyst activity but not equal to it. Due to severe diffusion limitations and heat transfer complications, which are typical for Fischer-Tropsch reaction, catalysts with very high activity may show quite low productivity if placed into a catalytic bed. The above-mentioned limitations and complications can be relatively easily removed if one uses a catalyst in the form of small micrometric particles diluted with thermally conductive neutral agent such as quartz sand or silicon carbide powder. The active sites of the catalyst would release a large amount of product under such conditions. However, the volume of such diluted bed V_{bed} would be too large and hence P_{FT} would not reach any significant level as is obvious from equation. So this work does not consider experiments with diluted catalytic beds.

Higher productivity means smaller reactor size and, hence, lower capital investment in XTL plant. Also higher productivity means that smaller amount of the catalyst needs to be exchanged for fresh one during regular reloading.

This work reports the results of the study devoted to the development of a fixed bed reactors with significantly increased productivity 240 to 400 kg/(m^{3}hr). The research includes:

- The detailed mathematical modeling of tubular reactor with fixed bed;

- Formulation of preconditions for higher productivity process, including requirements to the reactor design for pilot scale unit and requirements to the temperature and pressure of the process;
- The results of developing and laboratory testing granular catalyst capable of manifesting productivity higher than 240 kg/(m^{3}hr) in a fixed bed;
- The results of designing, building and starting up a scaled-up pilot GTL unit (15 L/day) with a highly productive Fischer-Tropsch tubular reactor.

The mathematical model describes steady state process occurring in a fixed bed of a Fischer-Tropsch reactor. The model allows estimation of thermal stability of a catalytic particles with internal heat generation and diffusion resistance of gaseous component.

This model was integrated into a computer software, which allows calculation and visualization of temperature profile along and across the reactor as well as pressure gradient, velocity vector field and the map of concentration distribution of components in the reactor.

All numerical results of mathematical modeling were compared with experimental data. The experimental data were obtained on two types of chemical reactors with fixed catalytic bed: a laboratory scale single tube reactor 0.25 meter long and a demonstration scale reactor 1.5 meter long.

The analysis of the calculations showed that a highly productive catalytic bed should include a catalyst with high thermal conductivity and advanced pore system. It was also shown that a chosen highly productive catalyst can manifest high productivity if aspect ratio of a fixed bed is high enough.

We developed a catalyst for a highly productive Fischer-Tropsch process in compliance with recommendations of the mathematical models. This is a cobalt-based catalyst, which is manufactured by impregnation of a pelletized composite thermally conductive support with cobalt salts. The catalyst composition and manufacturing procedure are described in more detail in the following patents: rus. pat. 2405625 of 10.12.2010, rus. pat. 2414300 of 20.03.2011 and rus. pat. 2414296 of 20.03.2011.

The results of testing the developed catalyst allowed us to design, build and start up a scaled-up pilot unit for modeling a complete XTL process. The unit includes a reactor of desulfurization; a reactor of syngas production and two parallel highly productive Fischer-Tropsch tubular reactors.

ONE-STAGE TECHNOLOGY FOR PRODUCTION OF CONCENTRATED ETHYLENE GLYCOL-WATER SOLUTIONS (AUTOMOTIVE ANTIFREEZE)

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Abstract

The reactor unit for One-stage technology for production of concentrated Ethylene Glycol-Water solutions is described. Such solutions could be useful for production of automotive antifreezes. The technology is based on the high selective hydration of Ethylene Oxide in the presence of heterogeneous catalyst – anion-exchange resin in HCO_3^-/ CO_3^{2-}-form. The mathematical model of reactor allowed evaluating of economic benefit related to decrease of steam consumption.

Introduction

Hydration of ethylene oxide is an industrial approach to glycols in general, and ethylene glycol (EG) in particular. Ethylene glycol is one of the major large-scale products of industrial organic synthesis, with the world annual production of about 20 million ton/y. Approximately 7% of total amount of EG is used for antifreezes production. Today about 95 % of all EG is produced by a noncatalyzed reaction. As it follows from numerous investigations [1-3] hydration of ethylene oxide catalyzed by anion-exchange resin is one of the most promising methods for ethylene EG as alternative for conventional industrial noncatalytic process. Catalytic method provides significant energy saving in comparison with noncatalytic one due to much higher selectivity. The main disadvantage of such a catalyst is it’s deactivation that consists of two undesirable processes: loss of catalytically active sites and catalyst’s swelling. In our previous works the models of the tube fixed bed catalytic reactor [4] and of catalyst deactivation [5] were elaborated. In the present work above mentioned models were used for simulation of One-stage technology for production of concentrated Ethylene Glycol-Water solution.

Results

The main parameters influencing on of the catalyst and its activity are temperature and concentrations of ethylene oxide and glycol. The first series of calculations were made for two types of reactor – isothermal and adiabatic. Process conditions were varied in the following ranges: temperature 80-100°C; initial concentration of ethylene oxide 3-10 % mass.; initial concentration of glycol 0-29 % mass. In each case selectivity, catalyst's capacity, catalyst's volume, catalyst productivity (kmole of glycol per m3 of catalyst per h) and catalyst consumption (m^3 of catalyst per kmole of glycol) were calculated. Results of simulation showed that adiabatic reactor is more favorable than isothermal. Finally the reactor unit for One-stage production of 38-40% solution of Glycols in water was proposed. Reactor unit consists of five consecutive adiabatic column reactors with distributed ethylene oxide input in each reactor and intermediate heat exchangers; initial concentration of ethylene oxide in each reactor is 5.5 – 7.1 % mass. These conditions provide selectivity of EG about 96-98 %, and catalyst consumption about 0.001 t of catalyst per 1 t of Glycols, and catalyst life time 4000 h.

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SIMULATION OF THE METHANE CONVERSION BY PARTIAL OXIDATION IN A POROUS MEDIUM REACTOR

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Conversion of natural gas is extensively used in industry. Usually, conversion is carried out at high temperature and imply energy expenditure not only for the endothermic stages of the methane conversion, but also for heating the reaction mixture [1]. At the same time, there is the problem of how to use the sensible heat of the hot gas. An option to reduce energy expenditure is provided by the process in the filtration combustion (FC) mode under superadiabatic conditions [2]. FC is an exothermic process, which proceeds in a two-phase systems under the conditions where gas filters through a porous solid material [3,4]. In FC, the conditions for superadiabatic heating may be achieved, when, owing to the interphase heat exchange, the inherent heat recuperation occurs and both porous medium and the gaseous products leave the hot reaction zone being substantially cool. In this work, using a detailed kinetic model, which also takes into account the heterophase reactions, we consider the partial oxidation of methane with admixing steam in a porous medium reactor.

We model combustion of methane/oxygen/steam mixtures using the two-temperature approximation, a model substantially similar to that used in [5]. The model includes energy conservation equations for the solid and the gas without a heat loss to the environment. The inert porous solid and the gas are considered as interpenetrating continuous media, each one characterized by its own temperature; the media being coupled through a convective heat transfer coefficient. The set further includes the equation of state for the gas and the species conservation equations. The model is one-dimensional. The equations set was solved numerically using the first order Euler method with an implicit difference scheme. For each time slice, the Newton iterative method was used and corresponding boundary value problem for the linearized system of equations was solved by the matrix sweep method.

The kinetic scheme of the methane conversion was construed consecutively starting from the mechanism of initial reaction stages. The kinetics of oxygen-steam conversion of methane in a combustion wave is described by a chain-branching mechanism. The initial stage of methane oxidation includes the initiation reaction $CH_4+O_2 \rightarrow CH_3+HO_2$ and two branched cycles. Further, the kinetic scheme was supplemented by the interactions of reaction products with radicals, reactions yielding the succession of radicals, which react with water, molecular reactions. The constants for the chemical reactions were taken from methane oxidation databases [6, 7]. The reactions of radicals with the solid surface yielding carbonaceous deposits and heterophase reactions of carbon with the oxidant species in the gas were included into consideration also. The simplest set of reactions for carbon on the solid surface includes those with oxygen, water, and carbon dioxide. So, the kinetic model including 137 reactions and 33 species was used.

The calculations for the propagation of the filtration combustion wave in the FC reactor were performed. The results of the modeling for oxidation-steam methane conversion showed that it is possible to perform a reforming of gas mixtures containing large excess of methane over oxygen to synthesis gas in the running combustion wave mode with a superadiabatic heating. Kinetic modeling for the oxygen-steam conversion of methane showed a distinctive two-stage mechanism of the reaction with a substantially slower conversion of steam. In all performed calculations, the self-consistent combustion temperature is such that the steam reforming rate remained low, the partial conversion of the steam achieved in the combustion wave was due to the reaction of steam with soot. Thus, steam reforming occurs down the gas flow from the combustion front, where oxygen is depleted, with the active participation of soot deposits on the surface of porous material.

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OP-II-11

DEVELOPMENT OF ALUMINUM ANODIC OXIDATION PROCESS FOR FUNCTIONAL COATINGS DEPOSITION

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The anodic oxidation of aluminum in the electrochemical reactors has been used since 1930s to produce oxide coatings on the surfaces of aluminum and its alloys for various applications [1]. Quite recently this technology was proposed by several research groups in Japan, Europe and USA for the formation of anodic aluminum oxide (AAO) as catalyst support in the microreactors of various shapes: plates and honeycombs [2], axial cylindrical channels [3] and vertical tips [4]. In the anodic oxidation process it is important to account for: mechanical, thermal and chemical pre-treatment of the sample; nature of the electrolyte; temperature distribution in the electrolyte and sample; electrical current density per unit area of the sample. These conditions influence the following properties: re-distribution of impurities and mechanical forces in the sample, structure of the barrier and porous layers in AAO, its growth kinetics and ionic transport in it [1-5]. Fig.1 shows example of the effect of electrolyte mixing conditions on the temperature and voltage variation for our flat sample made of Al51st alloy (dimensions 40.0*30.6*0.5 mm^3).

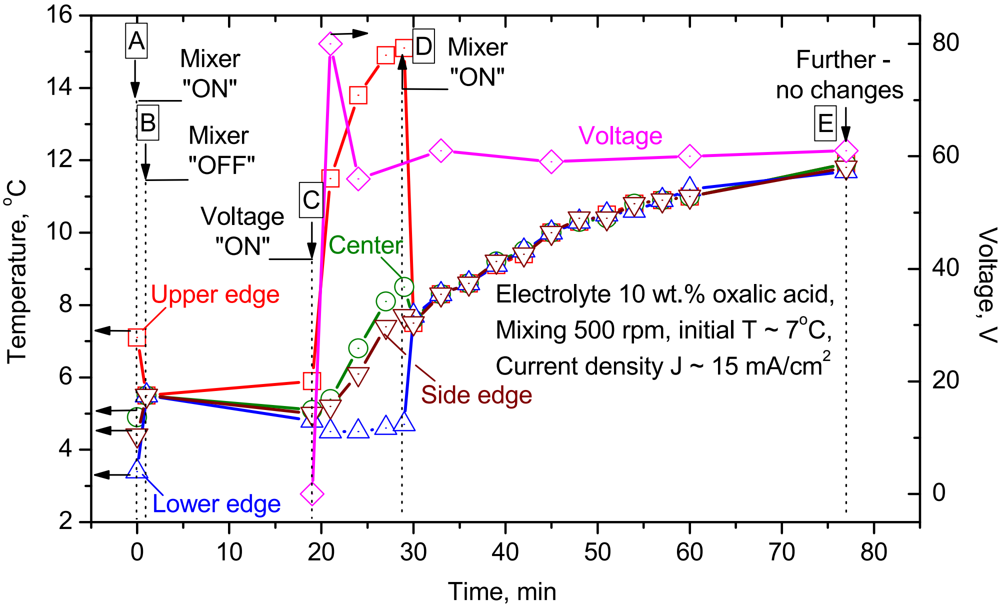

Fig. 1. Temperature and voltage variation during start of AAO formation on flat Al51st plate. Four thermocouples are located at the edges (upper, side, lower) and in the center of sample.

The best uniformity of temperature distribution across the sample gives possibility to more precisely control the growth rate and morphology of AAO, and in Fig.1 the most beneficial influence of mixing is seen starting from point D, when the voltage has been already applied and switching the mixer "on" resulted in the rapid equilibration of temperatures at all four measurement positions. For the series of plates with two different geometries, at optimized process conditions (AAO growth rate and porosity vs. electrolyte concentration, temperature and current density) we have established correlations between process time and AAO thickness. While the optical and scanning electron microscopies clearly show the presence of AAO layer, and textural measurements indicate bimodal pore distribution in it (diameters ~ 15 and 46 nm), the X-ray diffraction shows that anodized alloy structure is distorted compared to pure aluminum (relative to the main (111) peak, the intensity of peak (200) is lower and of (311) is higher), and that AAO probably consists of pseudo-boehmite phase. The method of AAO production developed in this work can be used to produce functional coatings for such applications as catalyst supports for the microstructured reactors [3,5], selectively permeable membranes for a number of catalytic processes [6] and synthesis of the wide nomenclature of nanomaterials [7].

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ISOMERIZATION OF n-BUTANE OVER Pd-SO_4/ZrO_2 CATALYST: PROSPECTS FOR COMMERCIAL APPLICATION

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Upgrading light HC in refineries and gas processing plants has increased in importance as new regulations affecting fuel quality are adopted in many countries. Increase in productivity of the refineries measured in octane-tons may be reached by means of light paraffin C_5-C_6 isomerization, isobutene (i-C_4) alkylation by olefins, MTBE synthesis. The last two technologies need boosting of isobutane production via n-butane (n-C_4) isomerization.

In 1959 UOP had commercialized technology known as *Butamer* process [1] for isomerization of n-C_4 to i-C_4 over Pt-modified chlorinated alumina catalyst (Pt-Cl/Al_2O_3). Fixed-bed catalytic process is performed in vapor phase at 120-200°C; to maintain the constant activity of the catalyst, toxic organic chlorides are continuously supplied to a raw stream. Process is highly sensitive to even smallest admixtures of contaminants in the raw, like allowable content of water ≤1 ppm, sulfur ≤1ppm, and fluorine ~0 ppm.

Catalysts for C_5-C_6 isomerization on basis of ZrO_2 modified by various anions are free from Pt-Cl/Al_2O_3 disadvantages and form the new generation of isomerization catalysts. Sulfated ZrO_2 Pt-modified catalysts (*Pt-SZ*) exhibit high activity for paraffin C_5-C_6 isomerization that is close to Pt-Cl/Al_2O_3 one [3]. However, low activity of *Pt-SZ* in n-C_4 isomerization was reported in [4].

Application of sulfated metal oxide catalysts in commercial n-C_4 isomerization has the obvious benefit, because no need in chlorine supply and lower standards of the trace contaminants in a raw can substantially simplify the technology and reduce the operating cost of i-C_4 production.

In this work, some specific features of n-C_4 isomerization over sulfated zirconia modified by Pd (*Pd-SZ* catalyst) were studied experimentally; and the prospects for commercial application of such a process were estimated. Catalyst samples were prepared in accordance with the procedure set forth in [5].

The influence of temperature, space velocity, pressure, H_2/n-C_4 ratio on the process characteristics was investigated in a lab-scale reactor under varying the parameters. The temperature and the $H_2/n\text{-}C_4$ ratio were found to have the major effect on the activity of *Pd-SZ* catalyst. It was shown that at the $H_2/n\text{-}C_4$ ratio within 0.15÷0.3 the apparent activity of *Pd-SZ* catalyst was high enough to fit the equilibrium degree of conversion of $n\text{-}C_4$ to $i\text{-}C_4$ at 140°C, that is, ~65% (Fig.1) .

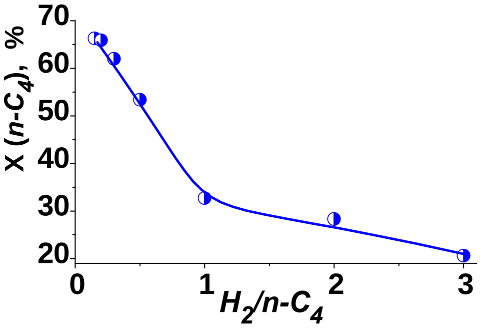

Fig. 1. Effect of molar ratio of $H_2/n\text{-}C_4$ on *Pd-SZ* activity. $G(n\text{-}C_4)= 1.5\ h^{-1}$, $T= 140\,°C$, *P= 23 atm, catalyst size 0.25÷0.5 mm.*

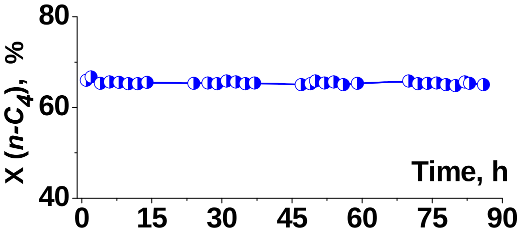

Fig. 2. Pilot testing of Pd-SZ in isomerization of n-C_4. H_2O= 20 ppm, H_2/н-C_4 = 0.2, T=140°C, P=23atm, G=1.5 h^{-1}, catalyst size 0.25÷0.5 mm

Water impact and the catalyst lifetime were studied in the pilot-scale setup. Endurance pilot testing of *Pd-SZ* catalyst in course of 90 hour showed its sustained operation at up to 20 ppm water vapor concentration without lack of activity (Fig.2).

The comparative activity tests were performed on the granules of *Pd-SZ* catalyst formed as 3 mm cylinders, 2 mm trilobes, and 0.25 ÷ 0.50 mm fines. Trilobe catalyst exhibited values of $n\text{-}C_4$ conversion 57.3% and $i\text{-}C_4$ selectivity 94.4%, that are close to the target specifications of the commercial process. By virtue of all received data, the main performance parameters of the reactor for isomerization of n-butane over *Pd-SZ* catalyst were estimated.

Our study of $n\text{-}C_4$ isomerization over *Pd-SZ* catalyst has revealed that attained $i\text{-}C_4$ selectivity was as high as 94-95% at near equilibrium conversion of $n\text{-}C_4$. Catalysts based on sulfated ZrO_2 modified by Pd may become an alternative to conventional chlorinated alumina catalysts in newly built or existing isomerization plants.

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OXIDATION OF *n*-BUTANE VPO CATALYSTS IN VARIOUS REACTORS: EFFECTS OF TRANSIENT REDOX CONDITIONS ON THE PRODUCTION OF MALEIC ANHYDRIDE

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The partial oxidation of n-butane to maleic anhydride (MA) is a very demanding reaction because vanadium phosphorus oxide (VPO) catalyst has to provide 14 electrons per formed MA molecule. The two-step redox mechanism applies, meaning that VPO may be seen as an oxide ion reservoir to be (partly) depleted. In the transient state the catalytic solid restructures because the V^{5+}/V^{4+} red/ox couple is faced with the butane/oxygen red/ox feed. At the steady state, the catalytic bulk is stable and rates of reduction and reoxidation of the surface are equal. Thanks to recent *in situ* investigations [1], the surface catalyst may be described as a vanadyl pyrophosphate core displaying multiplet $[V^{5+}/V^{4+}]PO_x$ sites on its surface. The atomic P/V ratio plays an important role in this concern, as well as on reducibility and catalytic performance [2]. P/V ratio is maintained slightly higher than unity in an oxidizing environment (1.8-2 vol% butane in air), typical of a fixed bed reactor, but is equal to unity for circulating fluid bed operation.

Special conditions or reactors can take advantage of the sensitivity of the surface red/ox properties. Transient redox operations, in which the catalyst is cycled sequentially between net oxidizing and reducing environments, or membrane reactors and CFB reactors are described.

Experimental. DuPont's commercial VPO catalyst (VPO particles encapsulated in porous silica shell) obtained by calcination/activation of $VOHPO_4{\bullet}0.5H_2O$ was used. The lab scale fluidized-bed reactor was operated under forced concentration cycling conditions (flow rate 40 mL/min STP, P = 1 bar, 500 mg).

Results and discussion. Transient data from the fluidized-bed reactor show that, irrespective of C_4H_{10}/O_2 ratio in the feed, butane conversion X_{C4} increases strongly with catalyst regeneration time (Figure 1). After 10 min of regeneration in air, X_{C4} increases up to 45% for C_4H_{10}/O_2 = 1.4/18.2 in the reducing environment. Upon decreasing O_2 content in the feed, the X_{C4} drop is as large as feed is fuel-rich ($C_4H_{10}/O_2 > 0.9$). The MA selectivity converges to 62−65% upon increasing O_2 in the feed, indicating that the effect of catalyst oxidation time on MA selectivity might be less critical in more oxidizing feed conditions.

These results will be compared with data obtained in an externally fluid-bed membrane reactor and in a pilot CFB reactor, in which the conditions are mostly oxidizing or reducing, respectively [3,4]. In the first case, the VPO catalyst is loaded inside a porous membrane tube into which C_4H_{10} is fed. An oxygen-rich gas fluidizes a powder on the shell side. Oxygen crosses the membrane wall and reacts with butane. Maleic yields are potentially 50% higher than in a conventional fixed-bed reactor and the reactant concentration operating range is much wider. In the CFB process technology, butane concentrations double that of fluidized beds are possible. The selectivity is relatively insensitive to gas-phase composition at 350°C and lies above 60 mol%, but it decreases in the most reducing $C_4H_{10}/O_2 = 9/4$ condition. The data show that there is a strong relationship between VPO catalyst reactivity, reduction feed composition and catalyst regeneration time, as well as with temperature. A strong dependency of maleic anhydride selectivity is observed on the feed composition at relatively short catalyst oxidation times (< 1 min), corresponding to operations in industrial reactors.

The amount of available surface oxygen species, which is supplied through reduction of gaseous O_2 and incorporation of O_2^-…O^{2-} onto or into the catalyst surface layers, decreases as the oxygen partial pressure in the feed decreases. The presence of gas-phase oxygen is critical to maintain high catalytic activity. Finally, there is no universal recipe valid for every reactor configuration. Indeed to maximize the commercial reactor performance, the VPO catalyst should be formulated to be adapted to the operating conditions (temperature, butane and oxygen partial pressures). Results show how the catalyst performance may be modulated by catalyst oxidation time or supply of oxygen, C_4/O_2 ratio and temperature.

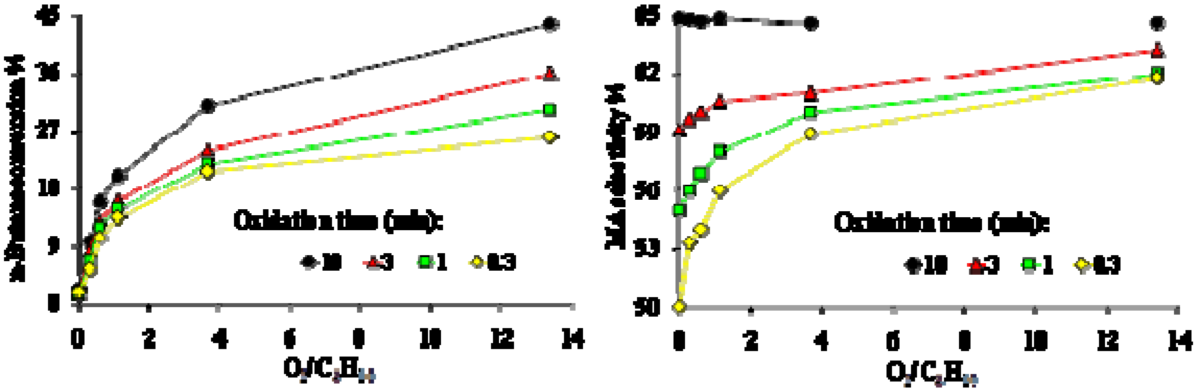

Figure 1. Butane conversion (left) and selectivity to MA (right) vs. reduction feed composition for different catalyst oxidation time (T = 380°C).

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ETHANE DEHYDROGENATION IN EXPERIMENTAL SETUP WITH ADDITIONAL RADICALS GENERATION

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Pyrolysis of ethane is generally conducted in tube furnaces. The radicals are generated on the hot inner walls of the reactor. The main idea of our experiments consists in pyrolysis realization via the radicals generation in the volume of the reaction mixture. Implementation of these conditions is possible with usage of the energy of the laser radiation [1-3]. Reagents heated through reactor walls up to temperature preceding to the beginning of pyrolysis and the radiation energy input directly into the gas created conditions for radicals generation in the reaction volume. Infrared radiation is efficiently absorbed by ethylene which is the primary product of the ethane pyrolysis. Ethylene via collision relaxation heats gas mixture up to pyrolysis temperature.

The lecture presents the results of the research of ethane dehydrogenation at the laboratory setup. The reaction chamber was a quartz cell with the inner diameter of 20 mm and the length of 240 mm. The chamber was equipped with two heaters one of them fulfilled the previous heating of the initial ethane – ethylene mixture up to 100 - 150 °C and another one, which length was 60 mm, supplied the delivery of the heat energy to the reaction zone. The radiation of the continuous CO_2 – laser, which wavelength was $\lambda \approx 10.6$ µm and the maximum radiation power was up to 130 W, was input through the ZnSe optical window to the chamber. The experimental data of the ethane conversion were obtained at the combined heating of the reaction mixture or at the heating via walls of the reaction chamber or laser radiation energy, separately. In the experiments, we varied the power of laser radiation, wall temperature, the volume fraction of ethylene in the initial ethane – ethylene mixture, and the irradiation time of the reaction mixture.

The dependence of the ethane conversion from the temperature is shown at the figure 1. When we heated reaction mixture via chamber walls the conversion of ethane was not above 5 % at the temperature range 520 – 630 °C and conversion was increased up to 38 %

at 710 °C. The combined heat of reagents provided the conversion of ethane to 20 – 30 % at the temperature 560 °C and the conversion was increased to 65 % at 710 °C.

The conversion of ethane was determined to be increased with the power of the laser radiation.

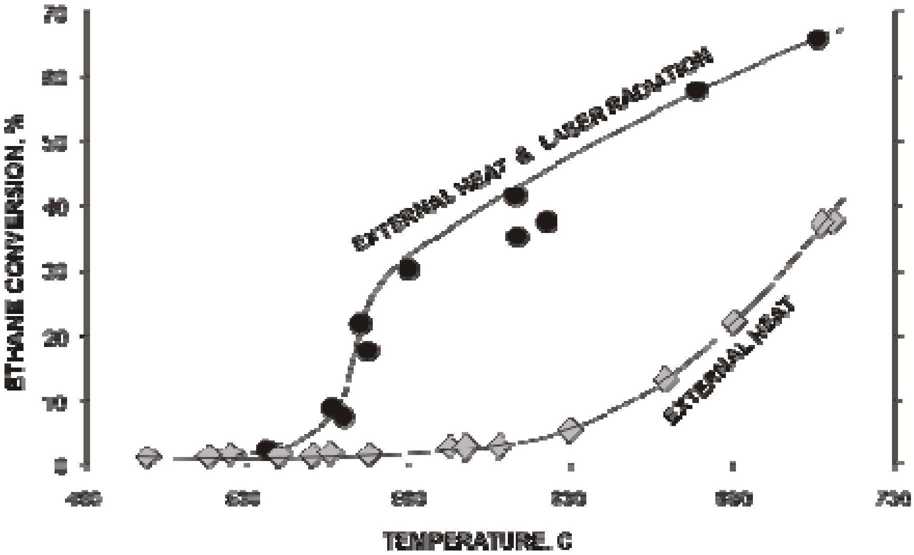

Fig. 1. Ethane conversion versus temperature for the combined heat of reagents or via reactor walls.

Thus, ethane dehydrogenation with the additional generation of radicals in the reaction volume efficiently occurs at reduced temperature of the chamber walls.

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DESIGN AND OPERATION OF PILOT PLANT FOR TWO-STAGE OXIDATION OF METHANOL INTO FORMIC ACID

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Formic acid is produced commercially by hydrolysis of methyl formate formed from methanol and carbon monoxide. Alternative gas phase technology of formic acid production by two-stage oxidation of methanol was developed by Boreskov Institute of Catalysis [1]:

$$CH_3OH + {}^1/_2O_2 \rightarrow CH_2O + H_2O \qquad CH_2O + {}^1/_2O_2 \rightarrow HCOOH$$

While the first reaction is well known and widely used in industry for formaldehyde production applying the oxide iron-molybdenum catalyst, the second one is brand new, formaldehyde being oxidized by air oxygen into formic acid on an appropriate V-Ti-O catalyst. The reaction proceeds at ambient pressure, 100-130°C, with selectivity of 85-90%. Effect of catalyst composition, nature of surface intermediates, kinetic behavior were studied intensively and published in [2,3,4]. These studies resulted in ascertainment of a reaction scheme and a kinetic model based on the detailed reaction mechanism [4].

Technology piloting was performed jointly by the academic institute and the engineering company possessing experience and expertise in design, construction and operation of formalin plants particularly. Since the first stage of methanol oxidation is similar to conventional formalin plants, main attention in reactor design was paid to the second stage of formaldehyde oxidation into formic acid.

Characteristics of industrial cooled tubular reactors for formaldehyde oxidation were determined by mathematical modeling for an inlet gas composition not exceeding a lower explosive limit. The goal was to minimize catalyst volume and to maximize tube diameter under restrictions imposed on formaldehyde conversion, pressure drop, hot spot temperature, hot spot temperature sensitivity and tube length. The following parameters were changing within a numerical procedure: gas velocity, cooling agent temperature, catalyst activity. Options of formaldehyde oxidation in two consecutive tubular reactors with different cooling agent temperatures and partial dilution of catalyst by inert material were studied as well. Chosen characteristics were used for designing a pilot plant with methanol input 2-3 kg/hour.

Methanol is pumped into a packed bed vaporizer fed by heated air delivered from an air line. The methanol-air mixture passes the first tubular reactor with 12 tubes filled by Fe-Mo-O catalyst. The reactor is cooled down by heat transfer fluid boiling in tube space. The output stream enters two consecutive tubular reactors loaded by V-Ti-O catalyst. One reactor has 18 tubes, another one 30 tubes. Temperature in the reactors is controlled by water boiling in tube space. Cooling systems of all three reactors have looped circuits, vapors being condensed in backflow condensers fed by cooling water. The stream after the third reactor goes to a two-stage condensation system. It is cooled down in shell-and-tube heat exchangers cooled by cooling water at the first stage and by antifreeze at the second one. The plant is equipped by a chilling machine. Condensate from two separators is collected in an accumulating vessel. The plant is fully automated and controlled by PC. Methanol and product flowrates are measured by electronic balances. Gas composition analysis is performed by GC connected to five points along a technological scheme by heated lines and is fully automated and controlled by PC.

Operation of the pilot plant has proved theoretical estimates and bench scale experiments. Selectivity of formaldehyde oxidation into formic acid is 85-87% at conversion of 98-99%. Methanol conversion is close to 100%. Content of formic acid in condensate is 55-56%. The rest is condensed water, residual formaldehyde and traces of methyl formate. Characteristics of different regimes, comparison of experi-mental temperature profiles with simulation results will be presented in the report.

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MICROREACTOR DESIGN FOR THE PROCESS OF ETHANOL DEHYDROGENATION

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The important direction of the chemical industry development is engineering of new alternative manufactures based on renewable sources of raw materials. Ethanol produced from plants and organic waste can become such raw material, in particular for synthesis of acetaldehyde by ethanol catalytic dehydrogenation. That has advantages compared to the technology used today, which applies ethylene as feed stream. But to realize the dehydrogenation process with high technological parameters new catalytic systems should be developed.

Recently new classes of heterogeneous catalysts such as the structured catalysts were studied. Those possess a number of advantages in comparison with conventional randomly packed beds - homogeneous distribution of a stream, low pressure drop. Moreover, fibers or cloth structured catalysts offer flexibility and endless forms that allow using them in reactors of a various constructions [1]. And catalyst design should be closely integrated with the reactor design.

To fully exploit benefits of a catalyst, the chemical reactor has to be designed and operated optimally, that is any mass and heat transfer resistances must be reduced, and contact time of the reactants must be well defined. All these can be reached using small reactor dimensions. Nowadays there are more than 50 chemical productions based on microtechnologies and it has become increasingly important in catalytic processes.

Thus, using achievements of a modern science, we tried to design a catalyst and a reactor for the process of dehydrogenation of ethanol to acetaldehyde.

Copper is known to be effective in reactions of dehydrogenation. So in this work Cu supported (5 wt %) catalyst was studied. Activated carbon fiber (ACF) was chosen as a structured support. The catalyst was tested in a plug flow reactor. According the research, the best results observed at 350°C with conversion of 20 % and selectivity of 98 %. Also reaction kinetics was studied and apparent activation energy was found to be 47 kJ/mol. These experimental parameters were used for the modeling calculations.

Fig. 1. 3D model of the reactor.

Further, considering an example of carbon fibers application [2], we offered a new design of reactor, representing a kind of assembly, consisting of several demountable details: top and bottom nuzzles, stream diffuser, fit rings and grids on which the catalyst settled down. The height of the reactor appeared to be 91 mm, external diameter was 80 mm. Taking into account geometrics and manners of fastening of some details, 3D model of the reactor was designed in SolidWorks CAD software (figure 1).

Then to make mathematical description of the model, inside reactor space should be defined. Moreover, to save disc storage and computation time only a quarter of reactor volume can be simulated, so the whole profile can be obtained considering the mirror symmetry approximation.

To describe ethanol flow dynamics Navier-Stokes equations and continuity equation were taken. To determine temperature distribution energy equation was used. Also to calculate the model, the following assumptions were made: input flow rate of 0,018 m/s was taken from the experiment in plug flow reactor, with wall flow rate equal to zero, inlet stream temperature was 350°C without additional heat, surface heat adsorption was as well considered. Besides reaction kinetics was included.

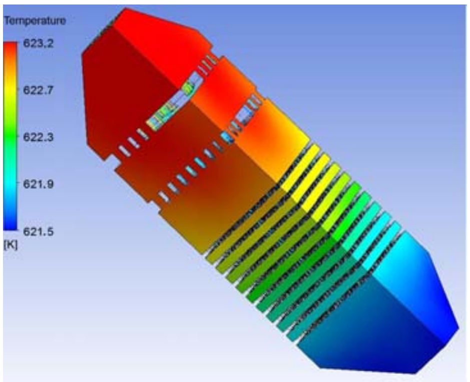

Fig. 2. Temperature distribution along the reactor.

With help of ANSYS software and finite element method being applied the model was calculated. As a result the diagram of temperature distribution was obtained. According the data presented on figure 2, the highest temperature drop didn´t exceed 2 K.

Thus, workability of the reactor for the process of dehydrogenation of ethanol with cooper on ACF catalyst has been shown.

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RAISING THE EFFICIENCY OF CATALYSTS FOR C_9-C_{14} ALKANES DEHYDROGENATION

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One of the modern sources for producing synthetic detergents for both domestic and industrial uses are the linear alkylbenzenes (LAB). LAB production itself has several stages, each using separate apparatus under different conditions. One of modern processes includes the following stages. Fistly, C_9–C_{14} alkanes are separated from kerosene cut in molecular sieves. Then clean alkanes undergo dehydrogenation on Pt catalysts, producing the alkenes C_9–C_{14}. By-products of dehydrogenation – dienes – are then hydrogenated to alkenes on Ni catalyst, and the alkenes flow comes to the alkylation reactor where LAB are formed.

The limiting stage is dehydrogenation. The efficiency of this stage defines the overall efficiency of LAB production plant. Modern catalysts for the process are PtSn/carrier systems, where the carrier can be γ–Al_2O_3 or aluminosilicate [1]. Catalyst can also contain spatial or electronic modifiers, like copper, indium and alkali metals [2–3]. The process requires temperatures in range 740–770 K and pressures in range 0.18–0.22 MPa.

One of the most efficient ways for optimizing the dehydrogenation process is using the mathematical modeling approach. The mathematical model and its software implementation is developed in Tomsk Polytechnic University to monitor and forecast the LAB production [4]. The model takes process unstationarity into account, as it considers side reactions of coke formation, cracking, izomerization and arene formation, further to dehydrogenation [5]. This is the advantage, as competition models are less adequate, especially when the contents of the raw stock are constantly changing.

Thus, the mathematical model allows predicting the service efficiency of certain catalysts and picking the most effective one for present industrial conditions. But new catalyst appear, having different contents and different efficiency. Authors conducted several experiments to define contents, specific surface area, pore structure and phase structure of several catalyst samples [6]. Correlation between this data and kinetic regularities of the process allowed to define interconnection that allows forecasting the efficiency of given catalyst without the need to conduct the full-scale industrial trial.

Another important problem connected with catalysts efficiency is regeneration of their catalytic activity after deactivation by coke. Generally, regeneration of dehydrogenation catalysts is not well-researched, and these catalysts are usually not regenerated. However, attempts were made to reactivate these catalysts beased on similarities of dehydrogenation catalysts to reforming catalysts that have similar contents. The regeneration procedure was divided into three main stages – high-temperature coke removal, oxidative chlorination and sulfuration of catalyst surface [7].

Two different ways of conducting the regeneration procedure were analyzed. It is shown that oxidative chlorination takes primary part in regenerating the catalytic qualities of Pt. Modernization option suggested that allows regenerating the catalyst at LAB production plant directly.

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OP-II-18

THEORETICAL INVESTIGATIONS OF METHANE CONVERSION TO HEAVIER HYDROCARBONS IN A PLASMA REACTOR

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Abstract

In this study, mathematical modeling of oxidative coupling of methane (OCM) to C_2 hydrocarbons (C_2H_6 and C_2H_4) over La_2O_3/CaO catalyst in a fixed-bed reactor operated under isothermal and non-isothermal conditions was investigated. The kinetic model proposed for OCM process consisted of 10 elementary reactions and 8 chemical species. In this process, methane and acetylene were the inputted feed and ethane, ethylene, propylene, propane, i-butane and n-butane were the output products. The amount of methane conversion obtained was 12.7% for the former feed, however, if pure methane was inputted this conversion rose to 13.8%. Furthermore, the plasma process would enhance the conversion, selectivity towards desired product and yield. In the present study, when methane and acetylene were fed at a molar ratio of $CH_4/C_2H_2=10$ to the reactor, the selectivity of C_2, C_3 and C_4 hydrocarbons was determined to be 30, 24 and 44% respectively. Concurrently, a higher yield was obtained for n-butane at about 3.9% and the minimum yield achieved for propylene was approximately 0.7%. A comparison between the thermal and the plasma process showed that the methane conversion and yield production in the plasma were higher than in the thermal process under the same operating conditions. On the other hand, product selectivity in the plasma process was determined to be lower than that of the thermal process. Finally, the results of the catalytic OCM and methane conversion processes in the plasma phase were compared with one another.

ORAL PRESENTATIONS

SECTION III

Chemical Reactors and Technologies for Emerging Applications

Processing of Biomass and Renewable Feedstocks
Environmental Protection and Utilization of Wastes
Production of Hydrogen and Green Fuels
Advanced Processing of Natural Gas and Oil

Section III-A

Processing of Biomass and Renewable Feedstocks

CATALYTIC FAST PYROLYSIS OF BIOMASS

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Fast pyrolysis is meant to convert biomass into a maximum quantity of liquids, that can be stored and transported easily, and used for energy, chemicals or as an intermediate for biofuels production. The process is characterized by a high rate of particle heating to moderate temperatures around 500°C, and the rapid cooling of the produced vapours to condense the liquids. This yields a maximum quantity of dark-brown mobile liquid (bio-oil) with a heating value roughly equal to that of the biomass, which is almost half the heating value of fossil fuel oil [1]. To improve the quality of crude bio-oil in relation to biofuel applications, and to reduce the upgrading costs, biomass pyrolysis can be carried out in the presence of suitable catalysts. Catalysis, either by adding catalyst particles to the reactor (in-bed) or by secondary conversion in the vapour phase (ex-bed), is applied for the removal of oxygen and the catalytic cracking of high molecular weight compounds in the pyrolysis vapours.

This research is focused on testing catalysts pre-screened by Albemarle Catalyst Company B.V. in Amsterdam, The Netherlands, in a dedicated mini-plant that allows variation of the catalyst loading and contact times while producing larger samples in continuous operation. The intention of the catalyst testing is to suppress coke and gas formation and to produce a fraction that can be used for co-feeding refinery units in the production of transportation fuels.

Catalytic fast pyrolysis experiments were carried out in a fully controlled continuous mini-plant designed and constructed by Biomass Technology Group B.V. (BTG) based on auger reactor technology. The mini-plant enables the production of larger bio-oil samples (typically 0,5 litre/run) suitable for a full characterization, even in the case of multiple phases in the bio-oil. Three types of biomass fast pyrolysis experiments can be performed in this system, namely; non-catalytic (only sand as heat carrier), in-bed catalytic and ex-bed catalytic fast pyrolysis experiments.

OP-III-A-1

It was decided that the mass balance closure must be between 95 % and 105 % for a proper interpretation of the results. The experimental reproducibility has been checked by repetition of several non-catalytic experiments under identical conditions. Of these tests the average yields (a.r.) are 68, 17, and 15 wt % for bio-oil, char, and gas, respectively. So far, catalyst "A" was tested both inside the reactor and in the outlet stream of the primary vapours, with an acceptable mass balance closure. In case of catalysis, the produced bio-oil was phase separated into a heavy organic fraction and a light water fraction. Next to the product yields in absence and presence of catalysts, an elemental-balance analysis revealed how much oxygen was removed from the bio-oil by using catalysts, as well as how much (useful) carbon and hydrogen was lost to the by-products. GC-MS analyses further clarified the effect of catalysis on the oxygen functionalities remaining in the oil as well as on the production of useful hydrocarbons.

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DESIGN OF CATALYTIC PROCESSES FOR BIOFUELS PRODUCTION FROM BIO-OIL AND PLANT OILS

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The new catalytic technologies of biomass processing should play a key role in the bioenergetics evolution. In Boreskov Institute of Catalysis the intensive investigations are carried out in the field of biodiesel production in the presence of heterogeneous catalysts, high-cetane fuels production from biodiesel and plant oils directly, upgrading of bio-oil – product of wood flash pyrolysis, production of bio-syn-gas and carbonaceous materials.

Development of heterogeneous catalysts for plant oils transetherification

The specificity of the work is development of new effective catalysts, adjusted to renewable feedstock. The one of developed technology is based on conjugated catalytic processes of transetherification and mild hydrocracking sequentially [1,2].

Main features of developed technology are:

- biofuel production of two types: biodiesel and green diesel;
- varying of biodiesel and green diesel yields depending needs;
- optimization of hydrogen consumption;
- energy-supply of both stages via burning of gaseous products, produced on 2nd step.

Catalytic characteristics of the technology include application of heterogeneous basic trasetherification catalysts under 200-220°C and 2.0 MPa and possibility of multiple catalyst regeneration for the first stage. For the second stage these ones comprise using of non-sulfided and non-noble metal catalysts, mild reaction conditions (300-340°C and 2.0 MPa H_2) and possibility of green diesel production with different cetane number via hydroisomerization catalysts application [3]. It was found (via XPS data) fresh $BaAl_{12}O_{19}$ catalyst has two forms of active components – strong-bond centers and weak-bond centers which were removed from catalyst surface during first cycle. After regeneration catalyst was showed constant activity in target process (Fig. 1).

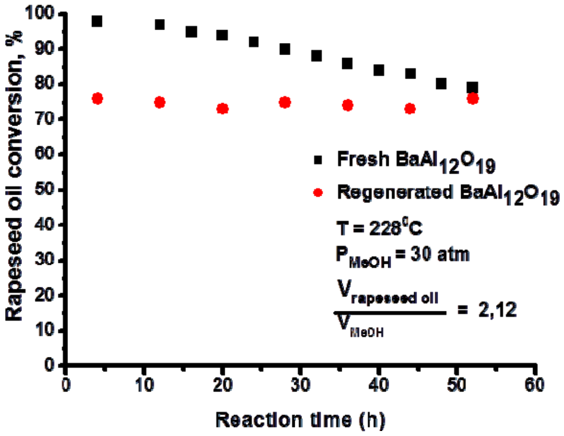

Fig. 1. Fresh and regenerated $BaAl_{12}O_{19}$ catalysts performance for transetherification of plant oils (biodiesel production). Catalyst was regenerated in the air atmosphere at 700°C for 3 h.

Bio-oil upgrading on Ni-based hydrotreatment catalysts

The bio-oil, which is a product of flash pyrolysis of grinded wood, is another perspective feedstock for the petrol production. However bio-oil cannot substitute traditional gasoline and diesel in the internal-combustion engines on its own owing to their lower operational properties. The main reason is the high oxygen content in above mentioned bio-fuels. The main goal of the hydrotreatment of bio-oil is to reduce the content of oxygen that is responsible for such negative properties of bio-oil as high viscosity, non-volatility, aggressivity, immiscibility with mineral oil, instability, and tendency to polymerization.

In general, the most promising approach in the hydrotreatment of bio-oil is a two-stage hydrotreatment at high pressures of hydrogen (5 – 10 MPa). In this case, the first stage at 150 – 250°C consists in the partial deoxygenation of bio-oil components, which increases the thermal stability of partially deoxygenated products during their further hydrotreatment at higher temperatures 300–380°C.

It should be pointed out that one cannot use traditional hydrocracking catalysts for oil-refinery at hydrotreatment of bio-fuels because of low sulfur content in original feedstock. Thus, the objective of the investigation is to develop non-sulfided catalysts for upgraded bio-fuels production. The obtained upgraded products can be used as additives to fossil crude-oil in the standard oil-refining.

This technological scheme of bio-oil upgrade process includes liquefaction of biomass, fractionation, hydrodeoxygenation (HDO) of lignin-rich fraction with following co-processing in petroleum refinery.

Indeed preparation and testing in target processes such binary catalytic systems has shown that developed mild hydrocracking catalysts permit to reduce oxygen content in bio-oils in one stage too from 45 wt% until 5 wt% at 320 – 350°C, hydrogen pressure 12–15 MPa [2].

It was shown (Fig. 2) that the increase in the Ni content in a sample (except *20.8*Ni) leads to an increase in the H/C ratio in the reaction products, which is a positive factor for the bio-oil hydrotreatment, because of the lower viscosity and molecular weight of the products. The increase in the ratio H/C indicates an increase in the activity of tested samples in hydrogenation [4]. The same effect was observed for HDO of anisole.

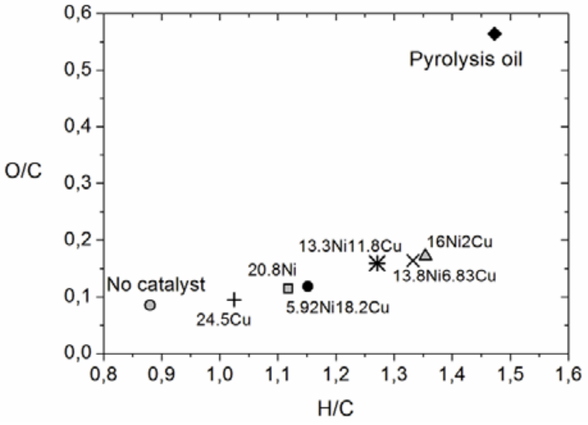

Fig. 2. Van Krevelen diagram for the products obtained in HDO of bio-oil over NiCu / Al_2O_3 catalysts at 11 MPa H_2 and temperatures 150 °C (for 1 h) and 350 °C (for 3 h).

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NEW INSIGHTS IN CATALYTIC HYDROTREATMENT OF FAST PYROLYSIS OIL USING HETEROGENEOUS CATALYSTS

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Introduction

Lignocellulosic biomass may be converted efficiently by fast-pyrolysis into pyrolysis oil, an attractive second generation liquid energy carrier[1]. The application of pyrolysis oils is limited due to some unfavorable properties like limited thermal stability, acidity, and relatively high viscosity. To extend the application range of pyrolysis oil, catalytic hydrotreating of the pyrolysis oil has been proposed[2]. With this technology, the properties may be improved dramatically and applications like for instance co-processing in existing oil refineries come within reach.

Results and discussion

Here we report an overview of our studies on catalytic hydrotreatment of pyrolysis oil as well as pyrolysis oil fractions using a wide range of heterogeneous catalysts. The performance of the various catalysts (activity, stability, hydrogen consumption) was critically evaluated and relevant product properties of the product oils (viscosity, coking tendency and elemental composition) were determined. A mechanism is proposed to explain the product properties as a function of process severity and type of catalysts.

Based on these findings, novel PICULA catalysts were developed which show excellent performance at relatively low temperature (< 250 °C) when compared to the benchmark Ru/C catalyst.

Conclusions

Novel catalysts have been developed for the catalytic hydrotretamnet of pyrolysis oil resulting in upgraded products with properties far better than those obtained with the bench mark Ru/C. Catalyst performance and product properties will be discussed in detail.

Acknowledgement

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SELECTIVE FRACTIONATION OF LIGNOCELLULOSIC MATERIALS USING SWITCHABLE IONIC LIQUIDS

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Introduction

Wood is a natural composite material consisting of cellulose, hemicelluloses and lignin as its major components. Any *selective* fractionation of lignocellulosic feedstocks into its pure components represents an important milestone in the development of efficient management of forest derived products thereby avoiding waste. Ionic liquids are increasingly becoming attractive as solvents for the fractionation of lignocellulosic materials due to their tuneable properties. However, the issues related to often unknown toxicity, frequently high viscosity, recyclability, stability and water intolerance of ionic liquids limit their widespread utilisation in wood fractionation. Switchable ionic liquids (SILs) [1] provide an alternative to traditional ionic liquids with significant potential in wood fractionation and recycling. SILs are composed of a superbase, such as an amidine, a hydroxyl containing compound and an acid gas in equimolar mixtures. Wood fractionation using SILs is a unique and novel approach towards selective fractionation of wood components. The effect of switchable ionic liquids in the fractionation of lignocellulosics biomass was studied in a batch and loop reactor. A physiochemical understanding of the performance of SILs for the selective fractionation of wood in different reactor systems was the focus in this study.

Reactor Setup and Operation

The loop rector was designed and constructed at Åbo Akademi University. The reactor with an inner volume of 30 ml, measuring 18 cm in length was connected to a 300 ml collecting vessel by stainless steel of inner diameter 9 cm. Heating coils were wrapped over the tubes while heating jackets in the reactor and collecting vessel ensured proper and even distribution of heat in the system. The SILs were circulated in the loop reactor by means of a gear pump (BVP-Z) at a flow rate of 500 ml/min. A schematic description of the loop reactor is shown in Figure 1. The picture of the batch reactor used is depicted in Figure 2.

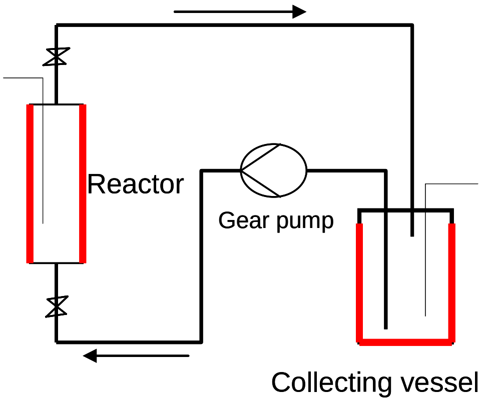

Figure 1: Loop reactor

Figure 2: Batch reactor

Birch chips (*Betula pendula*, 0.75 cm x 1 cm) were filled in the loop and batch reactors with equal SIL-to-wood ratios at 120 °C for 30 h. The SIL employed was synthesised from 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), diethanolamine (DEA) and CO_2. The up-flow circulation of SIL in the loop reactor ensured proper wetting of the chips while the batch reactor was employed in the absence of stirring. The solid phase was washed to remove the SIL, weighed and analysed for the sugars.

Analysis of the samples by acid methanolysis indicated that 55 wt-% of hemicelluloses were fractionated and dissolved from the wood in the loop reactor when treated with DBU-based CO_2-DEASIL. 40 wt-% hemicelluloses were dissolved in the batch reactor. The undissolved material was efficiently fibrillated and softened. The dissolved materials recovered from spent SIL after wood chip treatment were analysed as hemicelluloses and lignin. The forced flow of SIL through the loop reactor is thought to facilitate the dissolution of hemicelluloses, pectins and extractives in the SIL, permitting the flow of fluid through the pits of the wood. The continuous removal of the fractionated components from the wood also helps the dissolution process in the loop reactor as opposed to the batch reactor in the absence of agitation. Other reactors may also be added to the loop reactor in series to form a cascade system, facilitating the study of the kinetics of wood dissolution in SILs.

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OP-III-A-5

GREEN DIESEL FROM VALERIC ACIDS: EVALUATION OF Pd SUPPORTED ON ZrO_2 AND CeO_2 MODIFIED CATALYSTS IN CONSECUTIVE KETONIZATION AND HYDROGENATION

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For green diesel and jet fuel production from renewable organic materials such as C_5-C_9 carboxylic acids ketonization followed by subsequent hydrogenation [1] can be applied. Highly oxygen-functionalized biomass, namely levulinic acid, obtained for instance from glucose and cellulose, can be catalytically processed through the intermediate formation of γ-valerolactone to valeric acid and 5-nonanone. Various metal oxides deposited on the surface of inorganic supports were applied as catalysts for vapor phase ketonization of carboxylic acids [2,3]. Previously we have investigated the efficiency of more than 40 different oxide catalysts, which were mentioned in the literature as well as novel catalysts compositions (10%CeO_2/ZrO_2, 10%Y_2O_3/ZrO_2) in valeric acid to 5-nonanone conversion and have found that ZrO_2 and 10%CeO_2/ZrO_2 exhibited the highest activity and selectivity in decarboxylative coupling of valeric acid in H_2 atmosphere.

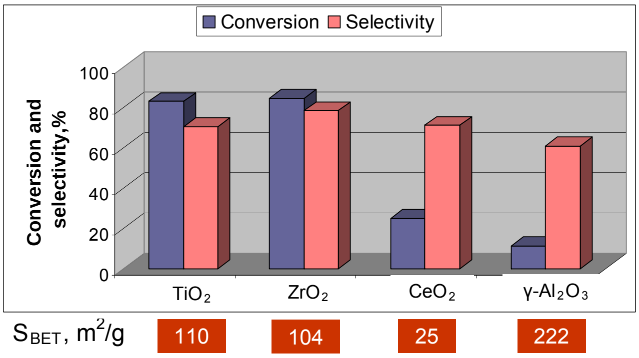

Fig. 1. Conversion of valeric acid and selectivity to 5-nonanone over metal oxides (628K, PH_2 = 1 bar, LHSV = 0,68 cm^3/(g·h)).

In continuation of this work the catalytic properties of Pd supported on ZrO_2, CeO_2 and modified CeO_2/ZrO_2 in consecutive valeric acid decarboxylative coupling and hydrogenation into nonane have been studied and the catalysts and supports structure, chemical composition of active component and electron properties responsible for catalytic activity have been elucidated by TEM, XPS, XRD (before and after the reaction).

The first step - decarboxylative coupling of valeric acid was carried out in the fixed bed flow reactor ($m_{catalyst}$=0.5g, fraction 0.25÷0.5 mm) at 573-678K under P_{H2} =1 bar with flow rates of 10-33 cm^3/min. The second step - hydrogenation of 5-nonanone was performed at 573-673K under P_{H2} =1-50 bar over 2%Pd supported on ZrO_2, CeO_2 and CeO_2/ZrO_2. The ketonization products were identified by Agilent Technologies 7000 GC/MS Triple Quad using silica fused capillary column Agilent HP-5ms (30m/0.25mm/0.25µm) (USA) and analyzed by GC with Stabilwax-DA (50 m/0.32 mm/0.5µm) (USA) at 373-473K with heating rate 10K/min (FID). Hydrogenation products were analyzed by Agilent Technologies 7890A (FID) equipped with a HP-5 (30 m/0.32 mm/0.25 µm) column and identified by Agilent Technologies 6890N with an Agilent Technologies 5973 mass selective detector equipped with a HP-5ms (30 m/0.25 mm/0.25 µm) column.

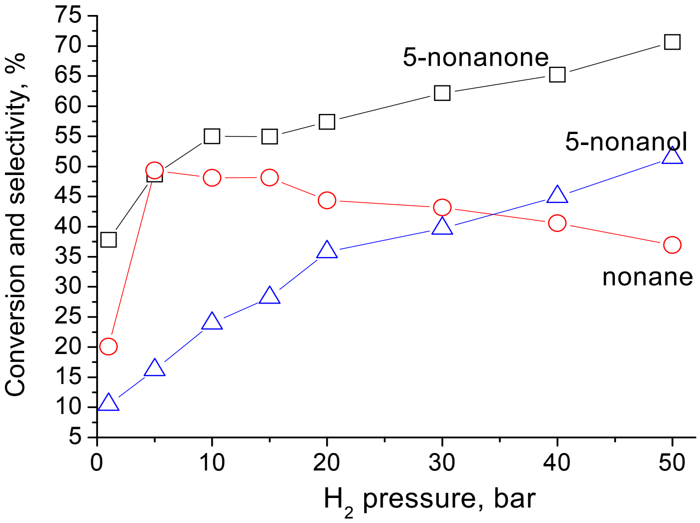

Fig.2. 5-Nonanone conversion and selectivity to nonane and 5-nonanol *vs.* hydrogen pressure over 2%Pd/CeO_2 (673K, LHSV = 16.7 mL/g min).

For all catalyst samples the effect of reaction temperature, hydrogen pressure, support calcination temperature, CeO_2 loading, and residence time on the conversion and selectivity to the desired products was investigated. From the mechanistic viewpoint it was shown that 5-nonanone into nonane hydrogenation proceeds via 5-nonanol over 2%Pd/CeO_2 with the maximum yield at PH_2 = 10 bar and 673 K (Fig. 2) while 5-nonanol was not observed in the case of 2%Pd/ZrO_2 at the same conditions. Correlations between catalyst structure and selectivity were established by TEM, XPS, XRD.

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OP-III-A-6

BIODIESEL PRODUCTION FROM RAPESEED AND USED FRYING OILS AND BIOBUTANOL. IMPROVEMENT OF COLD FLOW PROPERTIES

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In this study the process of synthesis of butyl esters from rapeseed oil (RSO), the most common oil feedstock for biodiesel production in Europe and used frying oil (UFO), as a cheaper raw material, using biobutanol, and potassium methoxide ($KOCH_3$) as catalyst, has been developed and optimized by application of factorial design and response surface methodology (RSM). Catalyst concentration was found to have the most significant influence on conversion. The optimum conditions were found to be a catalyst concentration of 1.1% and 0.9%, an operation temperature of 78°C and 80°C for rapeseed oil butyl esters (RSOBE) and used frying oil butyl esters (UFOBE), respectively, obtaining conversion rates of 96.86% and 96.54% with 6:1 biobutanol/oil molar ratio. Results show that the butyl esters produced using biobutanol as alcohol in the transesterification process improved cold flow properties in terms of cloud point (CP), pour point (PP) and cold filter plugging point (CFPP) without significantly affecting the other fuel properties. The resulting butyl esters can be used as a diesel fuel substitute, since it matches the European Biodiesel Standard EN 14214. In order to determine the effects of long storage on oxidation stability, the biodiesel samples were stored for a period of 12 months, the analysis of fuel properties: peroxide value (PV), acid value (AV), iodine value (IV) and viscosity (ν) have been applied in oxidation studies. According to the results obtained, the oxidative stability of RSOBE and UFOBE showed a sharp decrease over time.

Key words: Biodiesel, Cold flow properties, oxidation stability, Fatty acid butyl esters, Optimization.

ONE-POT AMINATION OF TERPENE ALCOHOLS OVER METAL OXIDES SUPPORTED Au CONTAINING CATALYSTS

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The amination of alcohols to complicated amines is of great importance in organic synthesis, granting access to valuable alkyl amines that are widely used as pharmacophores in numerous biologically active compounds, dyes, agrochemicals and functionalized materials. The development of an environmentally friendly catalytic route to such chemicals synthesis would be an important step towards a more green chemical industry. On the other hand, terpenes, extracted from biomass, are inexpensive renewable raw materials that have biological activity and are widely used in the development of new medicines. Tandem catalysis that enables one-pot multistep reactions holds a great potential for increasing the efficiency of chemical synthesis. A perspective one-pot way for the production of complicated amines consists of three steps: (i) the dehydrogenation of alcohol to aldehyde, (ii) the dehydrated condensation of aldehyde with primary amine to form imine via hemiaminal intermediate, and (iii) the hydrogen transfer to produce secondary amine (Fig. 1). It is important to note that hydrogen, generated by the step (i), can be used for the step (iii), so that neither O_2 nor H_2 is required for the alcohol oxidation or hydrogenation of imine. In addition, water is the only by-product [1].

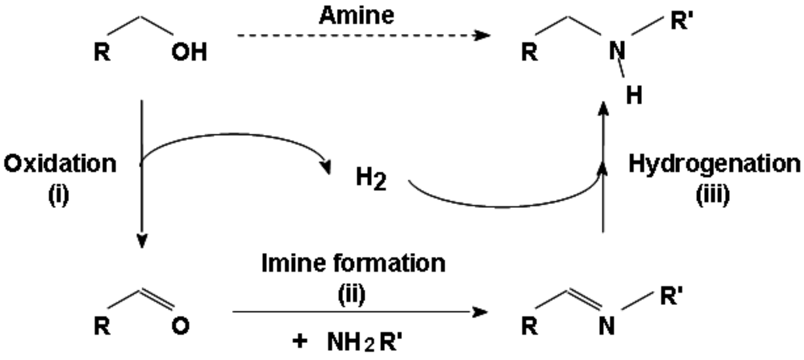
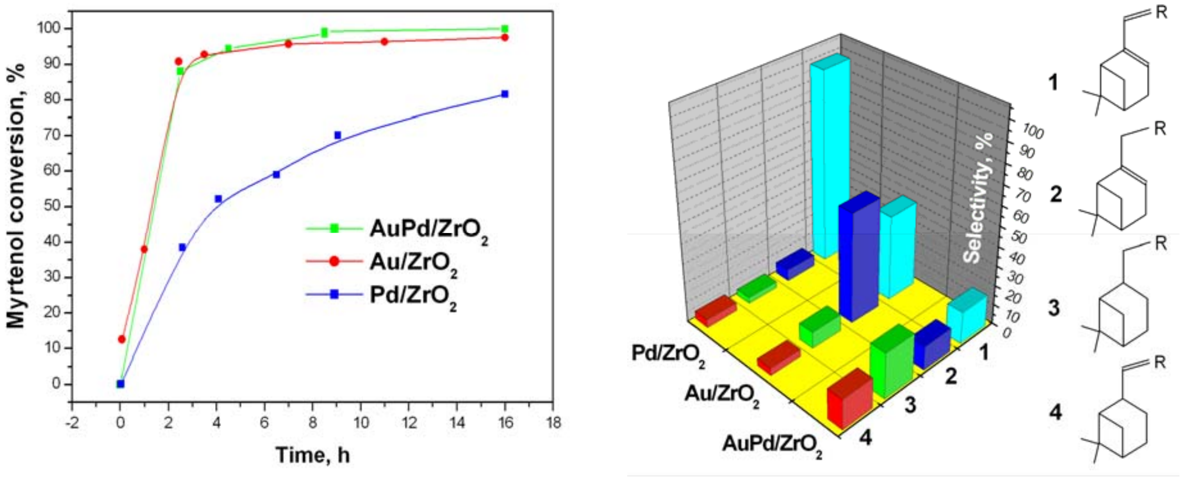


Fig. 1. Schematic view of the one-pot alcohols amination.

OP-III-A-7

The aim of this work is to study general peculiarities of natural mirtenol and carveol amination with aniline to corresponding amines over heterogeneous Au, Au-Pd and Pd (for comparison) catalysts and to tune selectivity to desired product through optimization of catalyst nanostructure, active component composition and support nature.

A series of nanosized gold catalyst samples including Au (3wt.%), bimetallic AuPd (3wt.% -1wt%) and Pd (1wt.%) samples over different metal oxides (ZrO_2, MgO, Al_2O_3, CeO_2, La_2O_3) are prepared by deposition-precipitation method. Myrtenol and carveol are used as model alcohol compounds with corresponding primary and secondary –OH groups. The activity and selectivity of the catalysts are tested in the liquid-phase at 5-9 bar nitrogen pressure in temperature region 100-180°C. The products were identified by GC-MS (column HP-5MS). The influence of catalyst temperature pretreatment under oxidizing or reducing atmosphere on catalytic activity in the reaction is studied. The products distribution and conversion were shown to strongly depend on active metal component composition (Fig. 2).



A **B**

Fig. 2. Myrtenol conversion dynamics (**A**) and selectivity to the main products (R=aniline) (**B**) for Au/ZrO_2, $AuPd/ZrO_2$ and Pd/ZrO_2. The reaction conditions: myrtenol 1 mmol, aniline 1 mmol, 180°C, 9 bar nitrogen pressure, solvent toluene (10 ml), M_{cat}=0.09 g.

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ORAL PRESENTATIONS

SECTION III

Chemical Reactors and Technologies for Emerging Applications

Processing of Biomass and Renewable Feedstocks
Environmental Protection and Utilization of Wastes
Production of Hydrogen and Green Fuels
Advanced Processing of Natural Gas and Oil

Section III-B

Feedstock Processing for Energetics

OP-III-B-1

FROM BIOGAS TO HYDROGEN: REFORMING PROCESSES DEVELOPMENT USING ADVANCED REACTION SYSTEMS

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Introduction

It is time for hydrogen energy and this opportunity should be seized by doing improvements and innovations in the existing technologies and processes as well as for developing a new ones [1]. Among many other possibilities, biogas reforming is a very interesting way for hydrogen or synthesis gas production. Biogas is considered a CO_2-neutral biofuel and if used as transport fuel instead of fossil fuels greenhouse gases (GHG), hydrocarbons, CO and particles emissions are reduced [2,3].

Experimental procedure

In this work biogas valorization – a renewable resource – to generate synthesis gas and hydrogen through dry reforming (DR) steam reforming (SR), oxidative reforming (OR) or tri-reforming (TR) processes was studied. Several Ni-based catalysts and a bimetallic Rh-Ni catalyst supported on magnesia or alumina modified with oxides like CeO_2 and ZrO_2 were used. For all the experiments, a synthetic biogas (molar composition: 60% CH_4 and 40% CO_2) was fed and the catalytic activities were measured in two different experimental facilities: a bench-scale fixed bed reactor system, FBR, and a microreactor reaction system, at 1073 K and atmospheric pressure. For all the processes different O_2/CH_4 and steam to carbon, S/C, ratios were used. Those catalysts which achieved high activity and stability in the FBR were impregnated in a microreactor to explore possible process intensification.

Results and discussion

The catalysts chemical compositions, which were determined by ICP-AES, were slightly lower than their intended ones. In addition, the textural properties, BET surface area and pore volume and diameter, of the calcined and degassed catalysts were evaluated. Through temperature programmed reduction, TPR, the reducible species formed during calcination step of the catalysts and the reduction temperatures were determined. Moreover XPS technique was used to evaluate the surface characteristics (oxidation state of the species formed, interactions, atomic ratios, etc) of the fresh and tested catalysts.

$Ni/Ce-Al_2O_3$, $Ni/Ce-Zr-Al_2O_3$ and $Rh-Ni/Ce-Al_2O_3$ catalysts were impregnated on microreactors. Comparing conventional and microreactor reaction systems, one order of magnitude higher Turnover Frequency, TOF, and hydrogen productivity, PROD, values were obtained by tested microreactors and similar activity results were achieved by all tested catalysts (Fig.1).

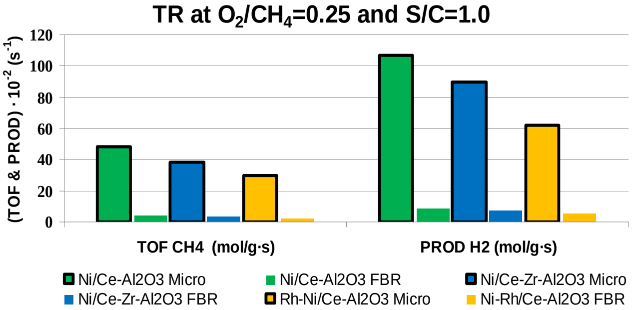

Figure 1: Comparison between microreactor and fixed bed reactor systems for biogas TR process.

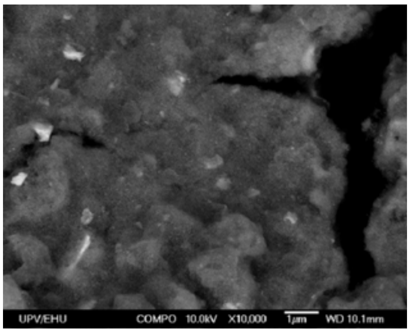

Figure 2: SEM micrograph of $Ni/Ce-Zr-Al_2O_3$ catalyst.

Finally, nickel dispersion, metal surface area and crystallite size were measured by H_2-pulse chemisorptions. In addition, SEM micrographs of fresh and used catalysts were taken as it can be observed in Fig. 2 for the tested $Ni/Ce-Zr-Al_2O_3$ catalyst.

Conclusions

For the monometallic and bimetallic catalysts, high CH_4 and CO_2 conversions were reached in the FBR, in which $Ni/Ce-Zr-Al_2O_3$ and $Rh-Ni/Ce-Al_2O_3$ catalysts reached the highest hydrogen production yield for biogas OR process at O_2/CH_4=0.25. Operating with microreactors a bit lower conversions were achieved being $Ni/Ce-Al_2O_3$ catalyst the one which reached the highest hydrogen production yield for TR process at O_2/CH_4=0.25 and S/C=1.0.

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Acknowledgements

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OP-III-B-2

HEAT SUPPLY UNITS WITH CATALYTIC COMBUSTION OF SOLID FUELS IN FLUIDISED BED

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The constant increase of energy demands combined with the growth of prices of all traditional fuels - oil, gas and coal - results in increased interest to previously unused low-quality fuels, including industrial waste and renewable biomass. It is important to take into account the enviromental aspect – preventing the toxic substances emission, especially while using low-quality solid fuels.

The common disadvantage of all conventional thermal-power systems involving fuel bed or flame combustion of solid fuel at a temperature range of 1200-1600°C is significant atmosphere pollution with toxic combustion products (NO_x, SO_x, CO, soot and benzpyrenes).

The problems of both the low-quality fuel combustion and decreasing toxic emissions were solved simultaneously with the creation of the technology of fuel combustion in the fluidized bed of an inert material [1]. The main advantage of the technology is the ability to reduce sulfur oxide emissions directly during the combustion by adding sulfur-absorbing limestone into the fuel. The other noticeable merit of the technoloy is the relatively lower (800—1000 °C) temperature, which is constant throughout all the combustion zone. Such temperatures result in less "thermal" nitrogen oxides production, no ash layering or melting, less equipment slagging and corrosion. The high heat transfer coeffitients are provided. This allows decreasing the surface of heat exchanger and expenses of furnace construction. The fluidized bed can be used for combusting low-quality fuels and waste containing high quantities of ash and moisture. The usage of cheap low-quality fuels lowers the self cost of heat production and the ability to incinerate combustible waste makes the fluidized bed furnace a fine device for harmful waste neutralization.

Nevertheless combustion in the fluidized bed of an inert material has a number of disadvantages. The furnace's output regulation span is severely limited. The fuel combustion occures within the fluidized bed as well as above the bed, thus requiring enlargement of furnace sizes. The level of toxic pollution still remains high. Combusting temperature of

800—1000 °C forces the usage of heat-resistant materials or furnace fettling. This increases the furnace start-up time up to several days. Furnace fettle tends to wear quickly within the fluidized bed. There is also a high possibility of layer slaggering in case of low-melting material presence within the solid fuel, which leads to large agglomerate build-up. Their removing is possible after a full furnace stop only.

A new technology of fuel combustion in the fluidized bed of catalyst was developed in the Boreskov institute of catalysis. The presence of catalyst during combustion eliminates many disadvantages specific to both flame and fluidized bed of inert material combustion technologies [2, 3]. Fuel combustion in the fluidized bed of catalyst particles allows combining heat release and transfer in a single fluidized bed at air/fuel ratio close to stoichiometric. Furthermore, the presence of the catalyst allows reducing the organic fuel combustion temperature to 350—750 °C, reducing the requirements for termochemical properties of construction materials and decreasing the level of erosive wear. The combustion process is complitely localized within the bed and does not occure above the bed of catalyst. This eliminates the possibility of secondary endothermic reactions resulting in toxic products in the freeboard zone.

Based on this technology a solid fuel catalytical pilot-scale unit for local heat supply of industrial and social objects with termal power of 3 GCal/h was designed. The main advantages of this technology are the ability to adjust the thermal power output in a wide range, and the ability to combust different types of solid fuels including low-quality fuel and waste. Catalytic combustion provides environmental safety lowering the dioxine content in the exhaust.

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OP-III-B-3

CATALYTICALLY CONVERTED ASSOCIATED PETROLEUM GAS – A SUITABLE RESOURCE FOR POWER GENERATION UNIT FEEDING APPLICATION

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Associated petroleum gas (APG) utilization is one of the key challenges for Russian north regions and territories of Arctic shelf especially relevant it terms of its emission reduction to the atmosphere. APG is a high-caloric gas of variable composition. It's typical composition is as follows (vol.%): 50-70 CH_4, 5-10 C_2H_6, 5-15 LPG, 1-10 N_2, 1-10 CO_2. APG could not be pumped directly into gas pipelines or used as a mono-fuel for power generation due to high content of non-methane fraction. Besides, it is unprofitable to build pipelines from Russian North and Siberia to industrial centers and to transport APG to them. The most reasonable way for remote oil wells with low gas-oil factor (<100 m^3 APG/ton of recovered oil) is to convert APG onsite into the fuel suitable for power plant feeding applications. For this purpose, it has been proposed to perform preliminary catalytic steam reforming of APG hydrocarbon components [1-4] to produce methane-hydrogen mixture, which can be used for power generation applications.

Laboratory studies of the reaction of steam reforming of light hydrocarbons into methane-hydrogen mixture were performed in a catalytic setup with the use a flow quartz reactor at atmospheric pressure. Experiments were performed using a model gas mixture of composition (vol.%): 11 C_3H_8, 22 CH_4, 67 H_2O. Each sample before reaction had been reduced in different types of reduction agents, namely, in a mixture of 8 vol.% H_2 and Ar, synthesis gas, or reaction mixture itself. To prevent condensing of water vapor, the reactor was initially heated to 120°C in Ar flow and then the reaction mixture was supplied. Ni- and Ru-containing systems were studied as the catalysts. The most active catalyst provided complete conversion of propane already at 280°C and GHSV 3100 h^{-1}.

Time on stream testing of the most active catalyst for several tens hours at 320°C and inlet GHSV 3100 h^{-1} proved stable production of the outlet methane-hydrogen mixture of composition (on dry basis) (vol.%): 4 H_2, 85 CH_4, 10 CO_2, 1 C_3H_8. At higher temperatures, the hydrogen concentration increased, that of methane decreased due to steam reforming reaction; propane was converted completely. A prototype catalytic converter capable of 10 m^3 APG /h was developed and tested using real APG. Conversion of LPG fraction and ethane was more than 95-99% during tests at 330°C.

Both initial and reformed APG were used for fuelling a power generation unit on the base of gas internal combustion engine MTES-30 (nominal electric power 36 kW).

In case of initial APG fuelling, electric power of the plant decreased by 8 kW (power loss ~22%), exhaust gas contained black smoke. When the power plant was fuelled by methane-hydrogen mixture produced by APG catalytic reforming, the engine power increased by 21% and attained the nominal value; the engine showed excellent dynamic and temperature characteristics, stably supported crank rotation frequency.

Thus, catalytic reforming of APG into methane-hydrogen mixture is a promising approach for solving APG utilization problem for the remote oil wells of the Russian north regions and territories of Arctic shelf.

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CONVERTION OF ASSOCIATED PETROLEUM GAS INTO METHANE-SYNGAS MIXTURES. REACTION MODELING AND REACTOR DESIGN

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Processing and utilization of associated petroleum gas (APG) is one of the key tasks ensuring the progress of gas-and-oil producing industry in Russia. A number of approaches to process gaseous hydrocarbons are available currently. One of the existing methods addresses APG processing at industrial-scale plants. This approach provides the most efficient and complete utilization of APG to produce high-value-added products. The use of physicochemical methods allows APG processing to dry gas supplied to trunk pipeline systems, natural gasoline, LPG for domestic needs and for use as a feedstock for producing valuable chemical products (synthetic rubber, plastics, high octane gasoline components, etc.). Gas processing plants most often use chemical methods for the conversion of gaseous hydrocarbons into liquid products – gas-to-liquid (GTL) processes. However, these methods require complex systems and high cost equipment, and worth only at industrial-scale APG processing (>1 BCM/year). Some of the above APG utilization programs are inappropriate for geographically remote or poor oil deposits, which unable to payback significant investments for the development of transportation and petrochemical infrastructure. Since oil fields in Russian North and Arctic shelf locate far away from industrial centers and cities and construction of transportation infrastructure comes highly expensive in these territories, the APG utilization approaches are focused mainly on generation of electric power, which can be used both for local needs and transported for long distances. Direct use of APG as a mono-fuel for power generation (gas engines, gas turbines) is limited by low methane content (low methane number), unstable gas composition, high coking and knocking risk that decreases the service life and causes engine damage. In order to increase methane content and, consequently, methane number of the gas mixture, APG heavy hydrocarbon components can be converted into methane-hydrogen mixture by a process which is similar to a pre-reforming step at hydrogen production from natural gas and refinery gases in petrochemical processes. In contrast to the known petrochemical process conditions (pre-reforming is performed at 400-450°C with high ratio of H_2O/C), this process is performed at temperatures not exceeding 350 °C with low H_2O content in the reaction gas mixture in order to prevent steam reforming of methane and obtain the highest methane concentration.

In this work, laboratory studies of the reaction of steam reforming of hydrocarbons into methane-hydrogen mixture were performed using APG-simulating methane-propane mixtures (mainly, mixtures of methane and propane were used for the APG modeling). Ni- and Ru-containing systems were studied as the catalysts. Detailed kinetic experiments were performed and the most appropriate reaction scheme was proposed. In the presence of water at low temperatures, the reaction of propane steam reforming proceeds predominantly; the main reaction products are hydrogen and carbon dioxide:

$$C_3H_8 + 6H_2O = 3CO_2 + 10H_2 \qquad (1)$$

As hydrogen appears in the reaction mixture, the exothermic reaction of hydrocarbon hydrocracking to produce methane occurs simultaneously.

$$C_3H_8 + 2H_2 = 3CH_4 \qquad (2)$$

In the presence of water, the reverse water gas shift reaction does not proceed at temperatures below 350^oC; all catalysts demonstrate low CO outlet concentrations:

$$H_2 + CO_2 = CO + H_2O \qquad (3)$$

In general, relative contribution of reactions (1)–(3) to the whole process can be illustrated by the temperature dependence of the outlet H_2/CO_2 concentration ratio.

For example, for Ni-containing catalyst this ratio at 200-230°C is equal to ~3.3 that proves predominant contribution of reaction (1). As the temperature increases, this ratio decreases rapidly to values below 0.2 at 290-330°C indicating predominant role of methane generating reaction. At further temperature increase, the H_2/CO_2 ratio increases again due to predominant contribution of reaction (1).

A prototype catalytic converter capable of 10-15 m^3 APG/h was developed and tested using real APG. Conversion of LPG fraction and ethane was more than 95-99% during converter testing at 330°C.

Acknowledgements

The work was performed using partial financial support by State Contract №P1015 in framework of FFP 2009-2013, and State Contract №16.516.11.6006 in framework of FFP 2007-2013.

OP-III-B-5

ENERGY AND EXERGY ANALYSES OF HYDROGEN PRODUCTION FROM DIFFERENT ETHANOL REFORMING PROCESSES

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Hydrogen is considered a clean energy carrier which can be used for power generation via fuel cell technology. It can be produced chemically from a wide range of fossil and renewable fuels. Among the various alternative fuels, ethanol is a very attractive green fuel as it is produced by the fermentation of biomass and easy to handle as a liquid fuel [1]. Nowadays, there are several ways to produce hydrogen from ethanol. A steam reforming is among the widely used processes due to its high hydrogen yield; however, this process involves a highly endothermic reaction and requires high energy supply. To minimize the external heat input, partial oxidation and autothermal reforming are alternative routes for hydrogen production [2].

Regarding the first law of thermodynamics, an energy balance can determine energy requirements in the forms of streams of matter, heat and work, but fails to provide accurate information on how efficiently the supplied energy is used in a system. This is due to the fact that such an energy analysis cannot identify the real thermodynamic inefficiencies associated with the energy conversion system. On the other hand, an entropy balance determines the entropy generation within the system, which is an indicator of its inefficient energy usage. However, since entropy values still fail to account for the quality of energy, the true thermodynamic value (quality) of an energy carrier is characterized by its exergy. Exergy destruction which is one of the exergy-based variables represents the exergy destroyed due to irreversibility (entropy generation) within the system [3]. The irreversibility is caused by chemical reaction, heat transfer through a finite temperature difference, mixing of matter, unrestrained expansion and friction.

In the present paper, the first and second laws of thermodynamics are applied to a hydrogen production system in order to investigate changes in its system operation. The energy usage in three different ethanol reforming processes, i.e., steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR), and the irreversibility resulting from various chemical reaction sets and conditions for each hydrogen production system are analyzed and compared. Effects of reactant feed ratio and operating reforming temperatures (600-1500 K) on equilibrium compositions of gaseous product are also studied.

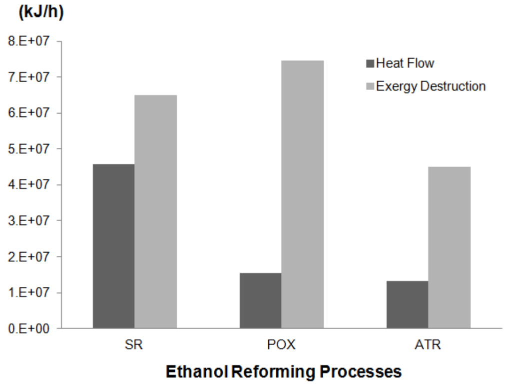

Fig. 1. Effect of ethanol reforming processes on energy demand and exergy destruction.

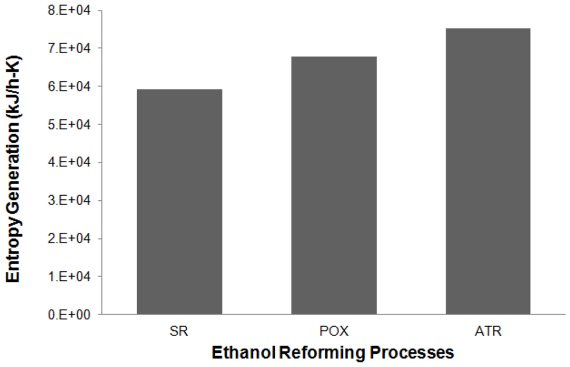

Fig. 2. Effect of ethanol reforming processes on entropy generation.

Fig. 1. shows the energy demand and exergy destruction of different ethanol reforming processes, which are operated at their optimal conditions giving the highest hydrogen yield. For the steam reforming process, the amount of energy is mainly consumed by an evaporation, heater and reformer. The energy requirement is strongly reduced when the partial oxidation or autothermal process is used for reforming ethanol to hydrogen. Although the partial oxidation requires less energy than the steam reforming, it causes higher exergy destruction because of the high temperature operation. Fig. 2. shows the entropy generation in the ethanol reforming processes. The irreversibility of each system is calculated from the entropy balance subtracted by the heat requirement. For this reason, the autothermal reforming of ethanol which requires less external heat input is the most entropy generation process. From the thermodynamic efficiency point of view, the steam reforming is the most favorable process to convert ethanol to hydrogen.

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OP-III-B-6

DEVELOPMENT OF PROCESS OF HIGH-ASH BIOMASS CONVERSION INTO CARBONACEOUS CATALYST SUPPORTS, ADSORBENTS AND MATERIALS FOR SUPERCAPACITORS

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High-ash biomass, containing mineral phase, as a rule - mainly of silica, is of interest as natural template-containing precursor of the porous carbons. Rice husk (RH) is the most widespread and available type of high-ash biomass containing 15 – 23 wt. % of ash which consists of more than 95 wt. % SiO_2 [1]. Due to high content of silica, RH is difficult to process waste and often discarding to dumps creating significant ecologic problems in rice-producing regions.

This work is devoted to desigh of process of RH conversion into porous carbon-silica nanocomposite materials and microporous carbons with specific surface area about maximal possible for carbons materials (about 2630 m^2g^{-1}) [2].

The first part of the work is carbonization of RH in fluidized catalyst bed (FCB) pilot-scale reactor with deep-oxidation catalyst (productivity on RH carbonization - 3 kg h^{-1}) at 465 – 600°C. This has allowed obtaining series of carbon-silica composite samples with A_{BET} = 170 – 220 m^2g^{-1}, mesoporous texture and SiO_2 content more than 50 wt. %. Investigation of RH and C/SiO_2 FCB465–600 by SAXS method showed increase of template SiO_2 phase particles size with the rise of carbonization temperature (Table 1).

Table 1 – Texture characteristic of RH carbonized in pilot-scale FCB reactor at 465, 550, 600°C and raw RH, and middle SiO_2 phase particle size in the samples

T, °C	A_{BET}, m^2g^{-1}	V_Σ/ V_μ, ml g^{-1}	Ash content, wt. %	SiO_2 phase particle size, nm, by SAXS
RH	-	-	19.5	4.2 ± 1.1
465	177	0.18/0.03	59	5.2 ± 2.7
550	217	0.20/0.03	71	5.8 ± 3.0
600	219	0.22/0.03	82	7.0 ± 3.6

Tests of C/SiO_2 FCB465 in comparison with Pd supported by Sibunit carbon material (also by Sibunit modified by SiO_2), showed that it is perspective catalyst support for Pd catalyst of the liquid phase selective hydration of C_2H_2 to C_2H_4.

Also C/SiO_2 FCB465 has appeared to be the most optimal precursor of microporous carbons, in comparison with C/SiO_2 FCB550 and 600, by alkali activation: with the use KOH, microporous carbons with A_{BET} more than 3000 m^2g^{-1}, V_Σ up to 3 ml g^{-1} and V_μ up to 1.9 ml g^{-1} were obtained. Estimation of their texture characteristics by non-Local DFT model, showed, that these materials possess A_{DFT} = 2400 – 2700 m^2g^{-1}, which is closely to maximal possible for carbons. The carbons series showed high adsorption capacity relating to H_2 – up to 6.3 wt % (at 77 K and 50 bar) and CH_4 – more than 40 wt. % (at 0°C and 60 bar).

Applying of pilot-scale reactor for KOH activation has leaded to obtaining of microporous carbon batches, with A_{BET} = 2700 – 3200 m^2g^{-1}, V_Σ = 1.5 – 2.3 ml g^{-1} and V_μ = 1.4 - 1.9 ml g^{-1} of up to 60 g of the carbon productivity per cycle. In the case of NaOH, a sample with lower texture characteristics and of more than 100 g quantity for cycle was obtained. Samples of the microporous carbons batches were tested on their properties as active materials for double-layer capacitors (Table 2).

Table 2 – Texture and electro-capacitive characteristics of microporous carbons batches obtained from C/SiO_2 FCB465 at 750°C (KOH) and 800°C (NaOH)

Sample	A_{BET}, m^2g^{-1}	V_Σ/ V_μ, ml g^{-1}	Ash content, wt. %	Electrolyte	Specific capacity, F g^{-1}
MC 4675KLP*)	2740	1.5/1.4	6.2	1M $LiBF_4$/ACN	160
MC 4675KLPII	3060	2.3/1.9	2.8	0.1M H_2SO_4	280
MC 4680NLP	2240	1.5/0.9	8.2	0.1M H_2SO_4	162

*) – jointly with Prof. S.P. Gubin and Dr. D.Yu. Kornilov, Akkolab Ltd., Moscow, Russia. A batch of 310 g of sample obtained in several-cycle operating time was used

Thus high-ash biomass, by the examle of RH, is perspective source of carbon-mineral composites and porous carbons, possessing attractive properties for catalytic and energy-effective applications.

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ORAL PRESENTATIONS

SECTION III

Chemical Reactors and Technologies for Emerging Applications

Processing of Biomass and Renewable Feedstocks
Environmental Protection and Utilization of Wastes
Production of Hydrogen and Green Fuels
Advanced Processing of Natural Gas and Oil

Section III-C

Environmental Protection and Chemical Processes

APPLICATION OF MATHEMATICAL METHODS FOR DERIVING THE RATE OF REACTION IN COMPLICATED REACTION MECHANISMS

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In the present paper, a systematic and straightforward method is proposed for deriving the reaction routes, the overall reactions, and consequently the rate of the reaction, based on the theory of complex reaction network by employing the mathematical concepts, which is also computerized using FORTRAN programming language. The catalytic cracking of n-butane over HZSM-5 is solved as a typical example using the proposed method. The theory of complex reaction network has not been applied up to the present to investigate the catalytic cracking of hydrocarbons.

Introduction. The theory of complex reactions [1-2] could be used in order to develop a kinetic model for the complicated mechanisms, especially over the catalyst surface [3-4]. It is not simple to determine all the reaction routes as well as the "basis of the routes", specifically when the number of the reaction stages exceed.

Mechanism of catalytic cracking of n-butane over ZSM-5 zeolites. Catalytic cracking is a very complex multi-component reaction that proceed through a complex network of reactions [5-6]. The mechanism of catalytic cracking of n-butane over ZSM-5 has been suggested as the following reaction steps [7].

1. $C_4 + Z \xrightarrow{k_i} C_4^{=}Z + H_2 \qquad i=1 \qquad r_i = k_i[C_4][Z]$
2. $C_4 + Z \xrightarrow{k_i} C_n^{=}Z + C_{4-n} \qquad i=2,3 \qquad 2 \le n \le 3 \qquad r_i = k_i[C_4][Z]$
3. $C_4 + C_n^{=}Z \xrightarrow{k_i} C_4^{=}Z + C_n \qquad i=4,5 \qquad 2 \le n \le 3 \qquad r_i = k_i[C_4][C_n^{=}Z]$
4. $C_n^{=} + C_m^{=}Z \underset{k'_i}{\overset{k_i}{\rightleftarrows}} C_{n+m}^{=}Z \qquad i=6,14 \qquad 2 \le n,m \le 4 \qquad r_i = k_i[C_n^{=}][C_m^{=}Z] - k_i^{'}[C_{n+m}^{=}Z]$
5. $C_n^{=} + Z \underset{k'_i}{\overset{k_i}{\rightleftarrows}} C_n^{=}Z \qquad i=15,21 \qquad 2 \le n \le 8 \qquad r_i = k_i[C_n^{=}][Z] - k_i^{'}[C_n^{=}Z]$

Theory, discussion, and application

1. The matrix of intermediates and the reaction routes

In the proposed procedure, the first step the suface species are re-ordered in a 3 dimensional matrix of intermediates, I (stage, intermediate, stoichiometry) according to their repitition. It was concluded that all the groups that results in reaction routes could be created by creating the closed loops started from the most repeated surface species in the matrix of intemediates.

2. The basis of the routes

It was concluded that if $N^{(1)}$ and $N^{(2)}$ include the common group $\nu_c s_c$ (c < s), then the sum of the absolute values of the stages that make $N^{(1)}$ and $N^{(2)}$ subtracted from 2 times the absolute values of the common stages is equal to the absolute summation of the dependent route stages, $N^{(3)}$ (dependent route). $\sum_{n=i}^{n}|\nu_n s_n| + \sum_{m=j}^{m}|\nu_m s_m| - 2\sum^{s}|\nu_c s_c| = \sum_{p=k}^{p}|\nu_p s_p|$

$$\begin{bmatrix}
(k'_{21}+k'_{14}) & 0 & 0 & 0 & -k_{14}[C_4^{=}] & 0 & 0 & -k_{21}[C_8^{=}] \\
0 & (k'_{20}+k'_{11}+k'_{13}) & 0 & 0 & -k_{11}[C_3^{=}] & -k_{13}[C_4^{=}] & 0 & -k_{20}[C_7^{=}] \\
0 & 0 & (k'_{19}+k'_{8}+k'_{10}+k'_{12}) & 0 & -k_{8}[C_2^{=}] & -k_{10}[C_3^{=}] & -k_{12}[C_4^{=}] & -k_{19}[C_6^{=}] \\
0 & 0 & 0 & (k'_{7}+k'_{18}+k'_{9}) & 0 & -k_{7}[C_2^{=}] & -k_{9}[C_3^{=}] & -k_{18}[C_5^{=}] \\
0 & -k'_{13} & -k'_{10} & -k'_{7} & 0 & (k'_{16}+k_5[C_4]+k_7[C_2^{=}]+k_{10}[C_3^{=}]+k_{13}[C_4^{=}]) & 0 & -(k_{16}[C_3^{=}]+k_3[C_4]) \\
0 & 0 & k'_{12} & k'_{9} & k'_{6} & 0 & -(k'_{15}+k_4[C_4]+k_9[C_3^{=}]+k_{12}[C_4^{=}]+k_6[C_2^{=}]) & (k_{15}[C_2^{=}]+k_2[C_4]) \\
k'_{14} & k'_{11} & k'_{8} & 0 & -(k'_{17}+k'_{6}+k_8[C_2^{=}]+k_{11}[C_3^{=}]+k_{14}[C_4^{=}]) & k_5[C_4] & (k_4[C_4]+k_6[C_2^{=}]) & (k_{17}[C_4^{=}]+k_1[C_4]) \\
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1
\end{bmatrix}
\begin{bmatrix}
[C_8^{=}Z] \\ [C_7^{=}Z] \\ [C_6^{=}Z] \\ [C_5^{=}Z] \\ [C_4^{=}Z] \\ [C_3^{=}Z] \\ [C_2^{=}Z] \\ [Z]
\end{bmatrix}
=
\begin{bmatrix}
0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ C_T
\end{bmatrix}$$

Figure 1: LU decomposition coefficient matrix.

3. Calculating the intermediates and the rate of the reaction

It is suggested that the correlations between the basis of routes and the rate of the reaction stages are organized in a system of equations with surface species as the variables. The system of linear or non-linear set of equations could be solved by employing the typical methods of LU decomposition, or sparse matrix solution method [8], respectively. This system is determined for the above mechanism using LU decomposition that is shown in Figure 1.

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CATALYTIC CONVERSION OF BIOGAS FOR PRODUCING VALUABLE PRODUCTS

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Sustainable development requires the new alternative and cheap energy sources and solving the problems of environment protection including the greenhouse gases effect. After the 70th energy shock, natural gas basically containing of methane is considered as an alternative to oil hydrocarbon raw material. At present, the methods of methane conversion for producing the various products of petrochemical synthesis are intensively developed. The production of methanol and liquefied synthetic hydrocarbons produced by steam methane conversion is the large-scale industrial process. Actually, methane can be attributed to the renewable energy and hydrocarbon resource, because of except natural gas the huge its amount is formed by bacterial biomass fermentation and during the organic sources processing. Methane is a main component of biogas – 50-87%, the rest is 13—50 % of carbon dioxide, small amount of hydrogen and H_2S admixtures. The list of organic wastes suitable for biogas production is rather wide. At present biogas is widely produced and used as fuel for production of electricity, heat or vapor, or as gaseous automobile/ motor fuel. Increasing biogas production in the world and practically inexhaustible resources for its production allow supposing that biogas can be used as alternative raw material not only for energy but also for production of petrochemical products such as motor fuel, oxygenates etc. by its conversion. Even now the biogas is produced in sufficient amount. Its excess can be converted into the petrochemical products. In future after exhaustion of natural hydrocarbon sources, the biogas can become one of alternative way for production of motor fuel and other petrochemical products.

In fact, the biogas itself represents a ready feedstock for dry reforming of methane because contains methane and carbon dioxide. Topicality of this direction is caused by involving both greenhouse gases - carbon dioxide and methane into the process for producing the final products through synthesis-gas. Dry reforming of methane is actively developed in the world. The main efforts are directed to creation of the effective coke resistant catalysts.

In the work, authors have used the biogas with varying content of CH_4 and CO_2 from 50-75 and 25-50% respectively. The biogas composition has been corrected by adding water steam in amount of 10-40 vol. % to get the reactive source with necessary atomic ratio of C/O~1/1. The bimetallic supported catalysts developed by authors have been used in both dry reforming and bi-reforming of methane. The processes were carried out at a flow quartz reactor supplied with the programmed heating and controlled feeding velocity under conditions: atmospheric pressure, space velocity - 1000 hr^{-1} and varying temperature from 300 to 800°C. The gaseous initial and final reaction products have been on-line analysed by the gaseous chromatographs. Liquid products were collected in a special cooling trap and analysed after reaction by using the GC.

The complete methane conversion has been observed at using a mix reached with carbon dioxide – 50 vol.% and adding 10 vol. % of steam under conditions: P=0.1MPa, T≤800°C and space velocity - 1000 hr^{-1}. The synthesis gas produced has a ratio of $H_2/CO=0.9$-1.0. Higher yield of hydrogen occurs at increasing water content from 10 to 40%, ratio of H_2/CO gets 1.1-1.6. Increasing methane content in a mix with carbon dioxide from 50 to 75% is accompanied with decreasing its conversion degree to 80-98%. Also negligible amount of oxygenates basically acids are formed.

It needs to note that if the high content of methane in biogas using for heat and electricity production is very important (developments in the field of biogas sets are directed towards decreasing content of other biogas components) then for dry reforming of methane the presence of carbon dioxide is required. Presence of hydrogen in biogas is favorable factor because of hydrogen is promoter of carbon dioxide decomposition that finally leads to decrease in process temperature. Also wet biogas can be used because it is possible involve water steam for combined steam. There is no necessity in drying of biogas because of water is initial reagent. That’s why biogas with reduced calorific factor (ill-conditioned) produced from any organic wastes can be used.

CATALYST DESIGN FOR REDUCTION OF NOx EMISSIONS

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Diesel engines are more fuel efficient and more robust than gasoline engines. The reduction of NO_x emissions from diesel driven vehicle is a challenging engineering and scientific task. Two recently commercialized catalytic processes for lean NO_x reduction are catalytic reduction (SCR) and Lean NO_x trap (LNT). SCR process, used commercially in stationary applications, eliminates the NO_x by a catalytic reaction with a reductant such as NH_3 or urea. The use of SCR for light-duty-powered vehicle is precluded because of the high price of the urea feed system. The LNT catalysts contain expensive precious group metal (PGM) components and NO_x adsorption components, and require frequent periodic shifts between fuel-lean and fuel rich modes. NH_3 is usually formed during LNT cycling and forms N_2 by reaction with adsorbed surface sulfates. The fuel itself or its partially oxidized products serve as the reductants. As NH_3 is readily formed during the feed on the LNT ad is easily trapped by the SCR catalysts. A combination of the LNT and SCR can shift part of the burden of the NO_x reduction from the expensive LNT catalyst to the less expensive SCR and avoid the need of on-board ammonia or urea feed. The optimal NO_x conversion and NH_3 selectivity in the LNT depend on the feed composition. For example, when no NO_x is present in the feed and a H_2 is the reductant the ideal performance obtained for a 50% NO_x conversion and 100% selectivity in the LNT.

Extensive research aims to determine the optimal catalyst composition and configuration that will provide the required NO_x reduction while minimizing the amount of expensive PGM in the LNT. One option is the LNT/SCR technology such as a sequential dual or multi LNT/SCR bricks. In these systems the LNT stores the NO_x and reduces it to a mixture of N_2 and NH_3. The adjacent SCR uses the NH_3 to reduce the NO_x that is emitted from the LNT. Another potential catalyst architecture that we studied is a dual layer in which a layer of a Cu/ZSM-5 selective catalytic reduction (SCR) catalyst is deposited on top of a Pt/Rh/BaO/CeO_2 LNT catalyst, The dual-layer catalyst had a higher NO_x conversion than the

LNT catalyst below 300 °C and a higher N_2 selectivity over the entire temperature range when H_2O and CO_2 were present in the feed.

Addition of ceria increased the LNT NO_x storage capacity, promoted hydrothermal durability and mitigated CO poisoning. However, the ceria decreased the high-temperature NO_x conversion due to the intensified NH_3 oxidation. The addition of the ceria enables adjusting of the tune the dual-layer catalyst performance. Use of a non-uniform ceria axial loading (zoning) of the LNT can increase its performance over that of a uniformly loaded loadand bio-molecular ed one. For example, a dual-layer catalyst with an increasing axial ceria loading led to the highest NO_x conversion for both low- and high- temperatures due to the beneficial interaction of the ceria and H_2. The ceria also mitigates the deleterious impact of CO, that may be formed by the water-gas shift reaction.

The low-temperature NO_x conversion of an aged dual-layer catalyst could be increased by increasing the SCR catalyst loading. However, at high temperatures the NO_x reduction was independent of the SCR loading. Optimization of the NO_x conversion in the temperature range from 150 to 400 °C requires adjustments in the ratio of the lean to rich feed duration and of the total cycle time. An important issue in the operation of the dual layer catalysts is to minimize the potential diffusion og precious metal from the LNT to the SCR layer, as this can deactivate the zeolite catalyst. It is expected that development of more advanced dual layer catalyst and optimization of the lean and rich feeds will enable a reduction in the required PGM load and a reduction in the fuel consumption.

MODIFIED KIT-6 AND SBA-15-SPHERICAL SUPPORTED Rh AND Ru CATALYSTS FOR N_2O ABATEMENT

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Introduction

Catalytic N_2O decomposition is considered the most effective and economical way to control N_2O emission. For this, noble metals particularly Rh containing catalysts, exhibit comparatively better activity [1], whereas, zeolites, alumina and silica have been used as catalyst support by many researchers [1-3]. Recently, our group used SBA-15-S (spherical type) and KIT-6 first time as support for Rh catalysts for N_2O decomposition [4]. However, KIT-6 supported catalyst was not so stable for long period of time. Therefore, in the present work, it has been focused to improve the supports (KIT-6 and SBA-15-S) by modifying the surface acidity by Al incorportaion and hydrothermal stability by post salt treatment. Moreover, different metals (Rh, Ru, Pd and Fe) have been tested on these modified supports in order to achieve a long time stable and more active optimized catalyst for the N_2O decomposition.

Experimental

Synthesis, characterizationand, and reaction of supported catalysts

KIT-6 and SBA-15-S support materials have been synthesized by following the procedure reported in our recent work [4]. Al incorporation and post salt treatment were performed by following the procedure of Hussain et al. [5]. Calcined KIT-6, SBA-15-S, and their Al and post salt treated Al modified supported (1 wt %) Rh or Ru or Pd or Fe catalysts were prepared by means of the incipent wetness method. The calcined catalysts were characterized by BET, SEM, EDX, NH_3-TPD and XPS. The activity of the prepared catalysts was analyzed by temperature programmed reaction (TPR), according to a standard operating procedure used in our previous work [4].

Results and discussion

Characterization and reaction activity of the supported catalysts

Interesting finding were observed by BET, SEM, EDX, TPD and XPS (not shown here) to evaluate the materials characteristics and correlate the activity.

OP-III-C-4

1 wt % Rh, Ru, Pd, or Fe supported on unmodified KIT-6 (K-6) as well as SBA-15-S (S-15) showed the following trend of activity for N_2O decomposition: Rh>Pd>Ru>Fe. However, after the Al or post salt treatment followed Al incorporation changed the activity trend and it was as follows: Rh>Ru>Pd>Fe. There was positive effect of Al or post salt treatment Al incorporation for Rh, Ru and Fe. However, the activity of Pd supported on modified mesoporous support materials was decreased. Therefore, the main focus is the comparison of supported Rh and Ru catalysts and the effect of post salt treatment and Al incorportaion as can be clearly seen in Fig. 1.

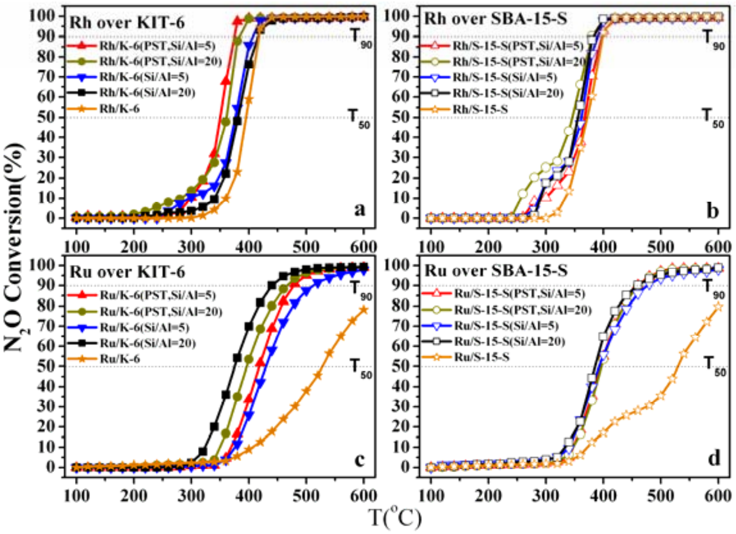

Fig. 1. N_2O abatement comparison

Comparing the activity, the modified KIT-6 supported Rh or Ru has shown more promising results for N_2O decomposition. It shows that its modification was synergized with the 3-dimensional pore structure of KIT-6 as compared to 2-dimensional SBA-15-S.

Conclusions

Compared to unmodified mesoporous supported catalysts, modfieid supported catalysts are very promising. Among Rh, Ru, Pd and Fe investigated, Rh or Ru are found to be the most active metals on the modified supports for N_2O decomposition. Rh/KIT-6 (PST, Si/Al=5) and Rh/SBA-15-S (PST, Si/Al=20) are the most promising optimized catalysts obtained in this study. Moreover, stability tests of the optimized catalysts as well the inhibiting and promoting factors are also in progress. The results encourage for further research and future applications of these materials. Therefore, final optimized catalyst will be soon investigated at pilot plant reactor for N_2O abatement at near real conditions.

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THE CATALYTIC INFLUENCE OF METAL CHLORIDES ON THE PROCESS OF OIL WASTE PYROLYSIS

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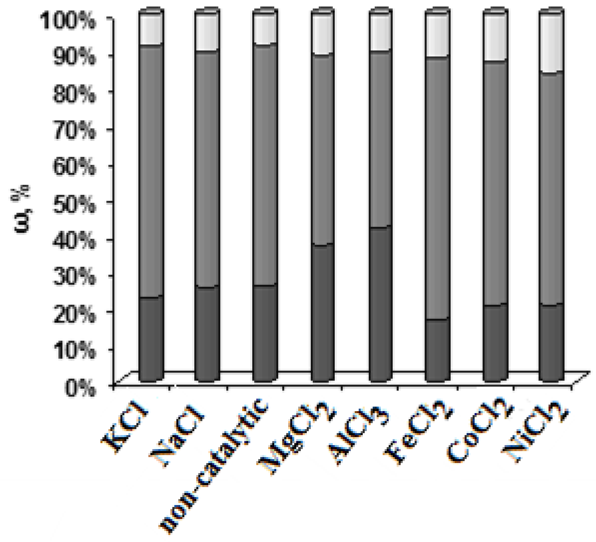
Recycling of oily waste by catalytic pyrolysis produces valuable gaseous and liquid fuels at lower temperatures of the process compared to traditional methods of thermal processing. Compared with other methods sludge pyrolysis has several advantages: low sensitivity to the composition of raw materials, closed recycling process and the ability to control the release of the final product that meets all the requirements of chemical industry. The use of catalysts in the pyrolysis process allows to increase the quality and yield of valuable products and reduce the temperature of the reaction process [1, 2].

In this paper we investigate the process of catalytic pyrolysis of oil-contaminated waste using as catalysts chloride of potassium, sodium, magnesium, aluminum, iron, cobalt and nickel. The pyrolysis process was carried out in an inert medium with a catalyst concentration 1 to 10% (by weight) based on the weight of the oil fraction. To study the catalytic process a model Caspian oil sludge was used with different oil content of the mass of sludge. The study of the pyrolysis of oil sludge was conducted in the temperature range 450-650 °C. The experiments were determined by the mass of solid, liquid and gaseous products of catalytic pyrolysis, depending on experimental conditions. The resulting gaseous products were investigated by gas chromatography and calorimetry. Using of alkali metal chlorides led to a slight increase in the conversion of oil sludge into gaseous and liquid products, while the use of cobalt and nickel chlorides leads to higher degree of conversion in the gaseous and liquid products (see Figure 1). Thus the use of cobalt chloride increases the mass fraction of gaseous and liquid products was 30% (by weight) compared to non-catalytic process. The experimental data showed that the use of potassium chloride increase the total heat of gaseous products combustion, while in case of magnesium and aluminum chlorides the increase in the proportion of gaseous products was observed simultaneously with increase of the mass of solid carbonaceous residue.



☐ – GAS; ▨ – LIQUID; ■ – SOLID.

Fig. 1. Mass fraction of catalytic pyrolysis product (10 % from mass of the sample) t = 500 °C

Using cobalt and nickel chloride as a catalyst increases the total heat of combustion of gaseous products as compared to non-catalytic process in 2.3 and 3 times respectively. The increase in the amount of methane and ethylene evolved during the pyrolysis of 2.8 and 5.2 times respectively compared with the non-catalytic process was observed for nickel chloride. Using the catalysts based on iron subgroup metal chlorides leads to reduce in activation energy for 30-50 kJ / mol, which confirms the effectiveness of these catalysts.

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NONTHERMAL PLASMA REACTOR FOR WASTE WATER TREATMENT

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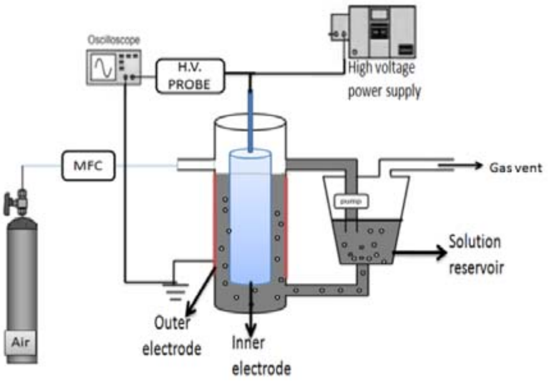
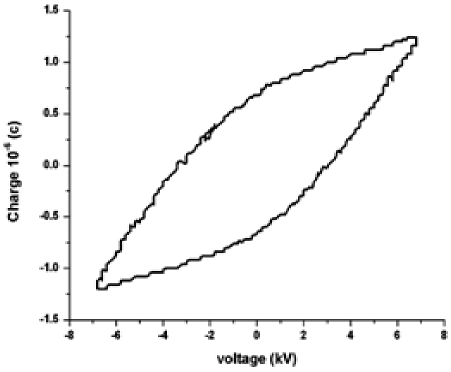
Water contamination is one of the most important issues and needs immediate attention due to the adverse effects of the contaminants on human and aquatic life. Dyes are toxic, carcinogenic and are typical discharge from paper and textile industries. Classical removal treatment processes are not effective as many of these methods may transfer the contaminant from one phase to another. There is an increasing interest in the application of nonthermal plasma in wastewater treatment. Advanced oxidation process based on dielectric barrier discharge at gas water interface has developed for the mineralization of wastewater containing model dyes. When the plasma discharge is initiated between two electrodes it interacts with water molecules that provide the necessary energy to ionize or dissociate water molecules generating active chemical species. Electrical breakdown in water produces UV radiation, shock wave, ions (H^+, H_3O^+, O^+, H^-, O^-, OH^-), molecular species (H_2, O_2, H_2O_2) and most importantly reactive radicals (such as O, H, OH) [1 and 2]. Among the active species, hydroxyl radical, atomic oxygen, ozone and hydrogen peroxide are the most important ones for the removal of dyes in water. OH radical, one of the most important oxidants, have a very short life time and are mainly generated from the direct dissociation of water molecules in the plasma region [1 and 3].



Experimental set-up



V–Q Lissajous figure at 50 Hz and 14 kV

The schematic diagram of the experimental setup is shown in Figure. The reactor is a quartz cylinder. Silver paste painted on the outer surface of the quartz tube acts as the outer electrode, whereas a stainless steel rod served as the inner electrode. The discharge length was 10 cm and discharge gap was 3.5 mm. The model dyes chosen were crystal violet, malachite green and methylene blue. The reaction progress was measured by using UV-Visible spectrometer, CO-CO_2 analyzer for mineralization, TOC analyzer for quantitative mineralization. Influence of various parameters like applied voltage, gas flow rate, concentrations of dye, addition of Fe^{2+} and pH was studied. Typical results indicated the best performance with oxygen bubbling during the reaction that may facilitate the formation of oxygen based species. Quantification of hydrogen peroxide and improved performance with the addition of Fe^{+2} via Fenton type reaction was observed. Confirmation of mineralization by TOC and infrared gas analyzers highlight the best performance of this technique. In addition, the high energy yield up to 88 g/kWh indicated the best degradation and the dye degradation followed first order kinetic behavior.

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Acknowledgements

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POSTER PRESENTATIONS

SECTION I

Advances in Chemical Reactors Fundamentals

PP-I-1

ANALYSIS OF POSSIBILITIES FOR THE INTENSIFICATION OF AMMONIA PRODUCTION

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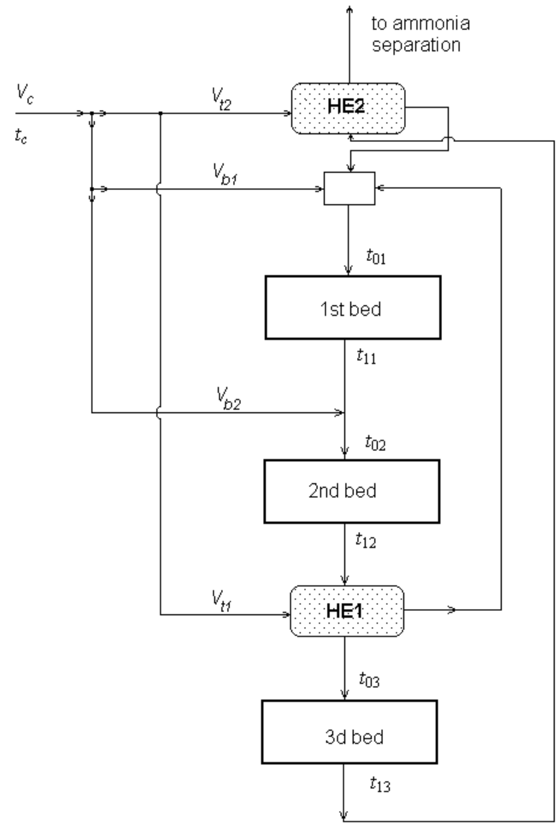
A process flowsheet of ammonia synthesis with the use of a reactor with three catalyst beds and radial feed has been studied. The schematic diagram of the reactor block is illustrated in the Figure.



Here: t_{0i}, t_{1i}, t_c is the temperature at the inlet and outlet of the i-th bed and that of the circulating gas, respectively; V_{t1}, V_{t2}, V_c, V_{b1}, V_{b2} are the flowrates of heat-transfer media in the heat exchangers, circulation gas and gases in by-pass lines, respectively; HE1 and HE2 denote heat exchangers. This scheme includes 2 cooling stages. Gas from the reactor after passing heat exchangers is fed to the first stage of ammonia cooling, where ammonia concentration is lowered to 10-12%, and from there to the second cooling stage, where its concentration decreases to 3-4%.

The second cooling stage is supplied with a fresh gas. There, water steam and other impurities are dissolved in liquid ammonia.

For reactor simulation we used the kinetic model of ammonia synthesis developed by Temkin and Pyzhev modified in that partial pressures were changed by fugitivities. A simplified computation method was applied to the ammonia cycle. The dependence of the circulation gas flowrate on pressure was taking into account on the basis of industrial data. It was admitted that the saturation pressure of ammonia vapor over liquid ammonia in the secondary condensation unit depends only on temperature. Each time catalyst activities on the beds were calculated from the industrial data on input and output temperatures of the corresponding bed and on the reactor output. The adjustment were performed by the minimization of the function S which is equal to the sum of squares of relative deviations between calculated and measured values of temperature and output, *QR*

$$S=\sum_i\left(\frac{t_{0i}-t_{0i}^e}{t_{0i}^e}\right)^2+\sum_i\left(\frac{t_{1i}-t_{1i}^e}{t_{1i}^e}\right)^2+\left(\frac{QR-QR^e}{QR^e}\right)^2$$

where the superscript ”e” relates to measured parameters.

Several ways for the improvement of ammonia synthesis processes have been reported. Among them are: decreasing ammonia fraction entering the column due to replacement of secondary condensation by the process of ammonia adsorption or absorption; removal of inert gases, ammonia recovery from purge gases; employment of catalysts allowing lower process pressures, etc.

The present work proposes different methods.

1) **Running the process at as low as possible pressure while maintaining predetermined production rate**

The problem consists in the determination of flowrates of coolants and gases in by-pass lines assuring optimum temperature profile over reactor beds. From mathematical viewpoint this is a multiparametric problem of nonlinear programming with constraints (material and heat balances and processing limits). The calculations show that for a unit with the capacity 71.5 t/h ammonia it is possible to lower pressure from 230.5 bars to 221 bars.

2) **Rising unit capacity at a given pressure**

The capacity may be increased owing to the optimum temperature profile which is achieved in the reactor due to the adjustment of the abovementioned flowrates. For pressure 230.5 bars it is possible to increase capacity by 6.06%.

3) **Fresh gas delivery directly to the entry of synthesis column**

Fresh gas passes through the column of adsorption cleaning from impurities and is fed to the reactor in the mixture with circulation gas. This enables decreasing ammonia concentration at the reactor inlet which results in the increase in the reaction rate and allows also to lower pressure at a constant capacity. Thus, for example, in an industrial reactor with catalyst activity equal to 0.821, 1, and 1 for the first, second, and third bed, respectively, pressure 240.3 bars is used to reach capacity 71.5 t/h. The supply of fresh gas to the reactor block entry gives the possibility to decrease pressure to 215.5 bars. The gain in the capacity of recycle compressor obtained due to lowering pressure is 1560 kW.

PP-I-2

MATHEMATICAL MODELING OF PROCESS OF STRUCTURIZATION POLYURETHANES BY COORDINATION COMPOUNDS

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It was considered the methods of obtaining columnar coordination compounds of copper that are active in reactions with isocyanate and urethane groups. The feature of these metal complexes is that the metal ions are arranged in a chain of atoms linked together by chloride bridges. It is established that the chain of exchange-coupled transition metal ions remains in the polyurethanes structured by metal complex compounds. This is the cause of stepwise decrease in the specific volume resistivity of the modified polyurethanes. It was researched behavior of metal-complex systems based on chlorides of copper in the reactions with UPTI. UPTI is an industrial prepolymer synthesized on the base of 1 mol polyoxitetramethyleneglicol and 2 mols 2,4-toluene diisocyanate.

The research spent with use of mathematical modeling process suggested that at relatively low concentration of the metal complex the urethane group dissociates to isocyanate and hydroxyl groups, while at high concentrations of the metal complex the isocyanate groups turn into carbodiimide groups. Suggested that at relatively low concentration of the metal complex the urethane group dissociates to isocyanate and hydroxyl groups, while at high concentrations of the metal complex the isocyanate groups turn into carbodiimide groups. The part of isocyanate groups is hypothetically consumed on the formation of the azoaromatic groups.

It was measured the dependence of the volume resistivity (ρ_v) of polyurethanes on the concentration of metal complex modifier. It turned out that the use of the developed metal complex system led to 10 000 times decrease of the volume resistivity ρ_v observed at low concentrations of metal complex (0.01%).

Acknowledgements

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THERMAL MODES OF THE COUNTERFLOW REACTOR OF REPLACEMENT

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Exothermal chemical processes in two-phase systems are used widely in the industry (the manufacture of explosives, mineral fertilizers, gas purification etc). Particularly, synthesis of the nitric fertilizers consisting of ammonium nitrate and ammonium sulfate is carried out in the counterflow reactors where the sulfur-nitric mixture is feeded from above, and ammonia bubbles from below.

Along with a choice of optimum operating modes of the counterflow reactors of replacement there is a problem of their safety from the point of view of runaway, i.e. occurrence of spontaneous thermal ignition.

In the present work on one- and two-temperature models the analysis of features of steady modes of the counterflow reactor of replacement with two-phase system of reagents gas – liquid has been carried out. The influence of velocity of movement of phases and interphase heat exchange on steady modes of simple exothermal reaction in a continuous phase (liquid) has been investigated.

We used following model. The liquid solution of reagent *A* (a continuous phase) is feeded with certain velocity *V* from above into the counterflow reactor of ideal replacement with given height. The gas containing other reagent *B* (a disperse phase) arrives in a bubble form from below. Velocity of disperse phase movement is defined as a difference between velocity of bubble movement in a quiet continuous phase [1] and velocity of continuous phase movement ($U - V$). Reagent *B* is extracted by continuous phase where it enters into simple exothermal second order reaction with reagent *A*.

Research of the temperature dependence of the maximum heating on the intensity of heat exchange with environment within of one-temperature model (the absence of heat exchange between liquid and gas) has revealed occurrence of two areas in a steady mode: low-temperature ("safe") and high-temperature ("dangerous") one. Between them rather extensive transient area is located. In other words, critical conditions of thermal explosion in considered system are not realized. In this connection it is reasonable to notice, that occurrence of critical conditions according to the theory of thermal explosion is directly connected with neglecting burning out that in our problem has no place. The situation considered by us is similar to degenerate thermal explosion, more likely.

The ability of the interphase heat exchange (two-temperature model) essentially influences on possible steady modes of the counterflow reactor of replacement. Subject to velocity of continuous phase movement *V* two types of steady modes are realized. At low velocities *V* we observed the steady modes in which the maximal heating of the continuous phase is localized near continuous phase input. With growth of the velocity *V* it moves to disperse phase input and maximum heating is localized here.

For gas phase at low velocities of counterflow the maximum heating is reached on the top end face of reactor, i.e on an input of a liquid phase. In process of the counterflow growth maximum heating of gas phase falls and drifts toward the interior of the reactor.

Interesting feature of steady modes of the counterflow reactor of replacement was found out when we researched another limiting case with the effective heat exchange between the phases. There are two modes: low-temperature ("safe") which is realized at the high velocities *V*, and high-temperature ("dangerous") one which is realized at low velocities *V*. The feature of the high-temperature mode is that in this mode the superadiabatic heating is reached. This heating essentially exceeds the heating observed in the absence of interphase heat exchange. In this case the full analogy with filtration burning of solid fuels takes place [2], namely, the disperse phase under the condition of the counterflow movement takes away a part of continuous phase heat and transfers it further to entering colder layers of a continuous phase.

Thus, the account of interphase heat exchange allows revealing new interesting features of thermal modes of the counterflow reactors. In particular, it appears that such heat exchange can cause rather essential, dangerous (from the practical point of view) heating and give rise to superadiabatic modes.

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USE OF THE COMPRESSION REACTOR TO PROCESS THE ASSOCIATED GAS

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For the past two decades, researchers in many countries try to invent a direct method of natural and petroleum gas conversion into heavy hydrocarbons bypassing a gas synthesis stage. The idea is to create a compact high-performance mobile processing unit to use it directly in the oil processing industry. Methods were developed to produce the synthesis gas and other products of associated gas from the natural gas in the chemical compression reactor - diesel engine.

Research team headed by A. Nikiforov, has worked out a method of a surface TECH-oxidation [3]. The covering resistant to the thermal cycling, is highly resistant to abrasion and heat. The coefficient of friction between the two coverings does not exceed $5 * 10^{-2}$. Surfaces in the reaction zone can withstand operating temperatures of more than 2000 K. One of the perspective applications of this innovation is to use a pair of compression "piston - cylinder" with the unique performance features for the conversion of hydrocarbons.

We have developed an original compression reactor to produce synthesis gas and for the controlled oxidation of associated gas to ethers and peroxy compounds. The reactor consists of piston and cylinder that are cooled. They are driven by a crank mechanism with tension rod. This mechanism provides a translational-rotational motion of the cylinder without lateral forces on the piston. The reactor has a system of measuring pressure in the reaction volume in real time. The construction provides the controlled regulation mechanisms of the cylinder upper dead point. These mechanisms have a response time of 0.1 seconds and an accuracy of 10 microns. Other mechanisms feed the reacting mixture in the reaction volume with a minimum response time of 0.5 ms. There is a system cooling the piston and the cylinder of the reactor in order to maintain an optimum gap between them. The working volume of the reactor is 0.1 to 0.6 liters. The optimal frequency of reactor operation is up to 10 Hz. The reactor is equipped with systems collecting reaction products, systems separating raw materials that didn't react to bring them back to the reactor entrance. Hardware-software system supporting the reactor provides on-line data and enables to manage the reactor mechanisms in order to optimize and to increase the reaction outcome percentage.

The set includes the electromechanical reactor startup system and the system collecting the excess energy released during the chemical reactions. Without lubrication as the surface to surface friction coefficient is low, there is no influence of lubricating materials during the process of chemical reactions inside of the reactor. The reactor construction enables to have a pressure above 100 atm in the chamber. This pressure in its turn enables a wide range of chemical reactions. The pressure control mechanism inside of the reaction volume provides information about the processes taking palace during the reaction. We have carried out a series of primary research of the process of the controlled chemical reaction in the chamber up to the stage of the gas mixture oxidation and generation of ether and peroxide compounds. Pentane was used as a raw material. Main interest is the start up of a chemical reaction in methane and methane mixture to higher hydrocarbons. The calculated curve of methane and methane mixture oxidation indicates the necessity to maintain the reacting mixture pressure at the level of 90 atm. According to evaluations the pressure increase transfers the reacting system from the mode of chain ignition to the quasistationary mode of branched-chain oxidation, providing a high reaction rate at relatively low temperatures. It also minimizes the influence of heterogeneous processes resulting in the formation of deep oxidation products.

The experimental facility enables working in the pressure range that would be unattainable in diesel engines. The necessary degree of compression is managed and maintained by the computer system with a feedback. That would be unavailable in the alternative systems.

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MODELING OF BUTADIENE POLYMERIZATION USING NEODYMIUM CATALYST COMPLEX

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The problems of obtaining and using neodymium polybutadiene are connected with structural features of the neodymium catalyst system. First of all, it is polycentricity of a catalyst, which contains several points of anionic coordination polymerization differing by their activity. Therefore, to investigate the possibility of rubber properties regulation by controlling the molecular structure is an important scientific and practical issue. In recent years, many researchers believe that most of the Ziegler-Natta catalysts have active centers of polymerization differing from one another by their kinetic parameters. In this study the mechanism of polymerization kinetics of 1,4-butadiene initiated by neodymium metal-complex system was identified.

The paper presents the kinetic scheme of the polymerization process. The model polymerization kinetics is represented by differential equations of material balance of reagents involved in the process and shows the changes in their concentrations over time. The system of equations of the model can essentially be solved for known kinetic constants for polymers of length $r = 1, 2, 3. . . n$. It is obvious that for the considered set of polymers the investigated system has large dimensionality. At the same time, there are efficient algorithms for solving systems of differential equations, which can reduce the order of the system. For the compact representation of the system of equations of polymerization kinetics, the method of moments is used. When the method of moments is used the system of differential equations is transformed into a closed form. It was found that under the selected conditions the existence of three different activity centers for polymerization in the catalytic system is most likely. The presence of different types of active centers in the considered system, established by mathematical modeling, is confirmed by the presence of three unshared peaks at the curve of molecular weight distribution (MWD) of polybutadiene obtained at the initial stage of polymerization. With increasing degree of monomer conversion the proportion of low molecular weight fractions decreases, while an increase of the undivided peak at the MWD curve in the region of high molecular masses is observed. Apparently, this is associated with the lower kinetic activity of the polymerization center, responsible for the formation of low molecular weight polymer.

MULTIPHASE FLOW AND DISPERSION OF H_2 IN THE SLURRY REACTOR

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A whole series of significant catalytic processes are carried out in a slurry reactor with multiple impellers [1]. The selective hydrogenation of sunflower seed oil is the characteristic example of such a process [2]. Three phases: liquid oil, solid fine-dispersed catalyst and gas phase hydrogen are introduced into reactor. A rate of mixing process of phases characterizes dynamic properties of multiphase system and unsteady catalitical reaction.

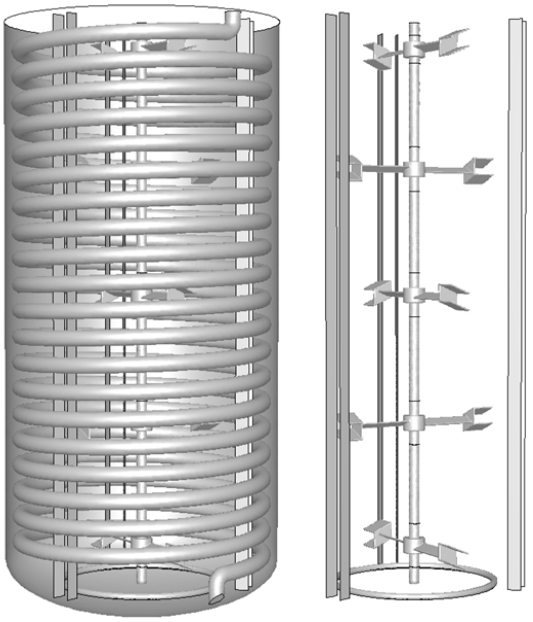
In the present work CFD simulation was used to predict the time evolution of gas phase distribution in the stirred tank with multiple impellers. Some data of the mediums and stirred tank are shown in table. The slurry reactor is shown on Fig. 1a. The main interior components is shown on Fig. 1b. The reactor has a cylindrical tank with ellipsoidal bottom shape, an axial drive top shaft with five-story impeller, three couples of upright flat baffles, spiral coil and nearbottom ring sparger. Each impeller has two blades, consisted of two rectangular plates. The impeller design is the simplified model of the Ekato Intermig impeller [3]. Design of top impeller is other than that of underlying four impellers. Location of top blades has a mirror position relatively underlying blades.

Tank diameter	m	2.0
Liquid volume	cub. m	12
Number of impellers		5
Number of blades		2
Impeller diameter	m	1.3
Impeller rotation speed	rpm	100
Liquid density	kg/cub.m	810
Liquid viscosity	kg/(m*s)	0.049
Solid particle diameter	m	0.0001
A specific density of solid	kg/m^3	2000
Volume-weighted average of volume fraction of solid		0.001
Mass flow rate of H_2	kg/s	$2.3*10^{-4}$

The CFD code was the Fluent software (Release 6.1-6.3). There is an unstructured, finite-volume, computer code used the pressure-based solver in our case. The model of slurry reactor was built and meshed using the software package GAMBIT. The 3D grid elements of control volume were tetrahedral.The total number of control volumes was equal $N=4.67x10^6$. The mixture model of multiphase flows from the Euler–Euler approach was applied to dilute gas-solid–liquid medium. In the mixture model the phases was treated as an interpenetrating continua and the concept of phasic volume fraction was introduced. The standard k–ε model of turrbulence was used [4]. Sliding Mesh Model was used to obtain time depending solution.

The preliminary result is shown on Fig. 2. The axial distribution of gas phase hydrogen was plotted for time from 0 to 1.0 second of mixing process. Hydrogen was injected into slurry tank throught nearbottom ring sparger with set of holes ∅2x10^{-3} m. The total area of hydrogen inlet was equal S_0=0.09366m. The mass flow rate of hydrogen was equal Q=2.3x10^{-4} kg/s.

The data on Fig.2 shows that gas-liquid mixing process has a sufficiently rapid nature in the slurry reactor. The trace of hydrogen arises on top surface of liquid during first second of mixing.



a) b)

Fig. 1. a) the slurry reactor. b) design of five-story impeller, flat baffles and near-bottom ring sparger.

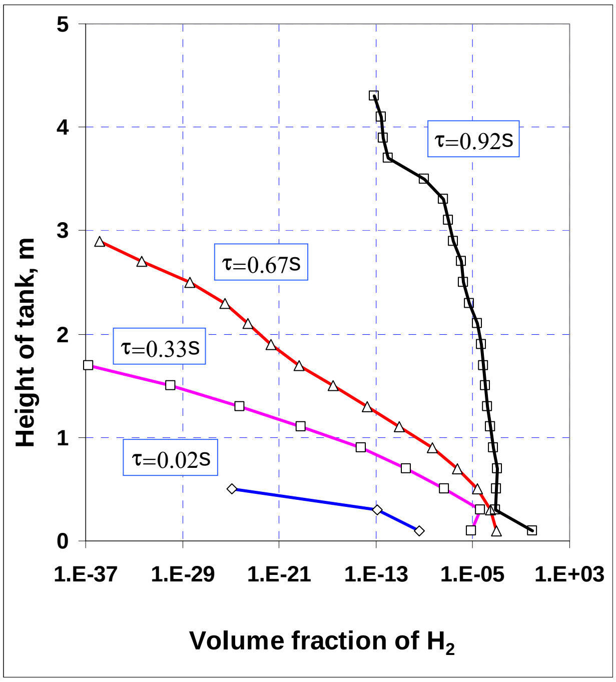


Fig. 2. The time evolution of axial distribution of gas phase (H_2).

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PP-I-7

ON THE POSSIBILITY OF PLASMA-CHEMICAL SYNTHESIS OF HEAVY HYDROCARBONS IN A FLOW WITH CLUSTERS

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Many research groups have repeatedly attempted to use a weakly ionized plasma flows to initiate reactions leading to the processing of volatile hydrocarbons (methane, ethane, etc.) in "severe", ie liquid under normal conditions. They used different types of electrical discharges, plasma torches, and accelerators. First of all, these efforts have stimulated the obvious advantages of gas-plasma flows. This is a huge cross-sections, as a consequence, the possibility of accelerating the conversion of hydrocarbons and, in turn, is a compact device with high performance.

But so far, all these advantages successfully implemented only on the first stage of the process. Radicals necessary to start the synthesis, formed successfully, but to organize an efficient synthesis of heavy hydrocarbons in these conditions have not yet succeeded [1].

Over the years, we investigated the possibility of a different approach. It is the formation of clusters in a supersonic stream containing certain proportions of light hydrocarbon molecules and atoms of the carrier gas - argon, and the subsequent "merging" the resulting clusters by electron impact.

Our pilot studies showed the following:

- varying the composition of the initial mixture and the parameters of inhibition can effectively manage the size, composition and structure of the clusters. Were obtained by multi-clusters, whose properties can vary from an amorphous state to crystal [2];
- Irradiation clustered flows of mixtures of methane and other gases by fast electrons leads to the formation of heavy hydrocarbons (up $C_{10}H_x$ inclusive). When added to a mixture of oxygen were detected alcohols and aldehydes. And these mass-spectrometric measurements in the flow correlated with the results of the chromatographic studies of samples collected at cryogenic trap [3];
- the experimental conditions in which such conversion was observed, similar to those in which the means of spectrometric observations clustered in supersonic flows of gas mixtures, activated by an electron beam, optical effects are observed - an anomalous

increase in emission intensity on individual atomic transitions in the carrier gas and the lifetime of the emitting states. This can only be explained by the formation of crystal-like structures formed in the flow of the clusters [4].

Thus, the efficiency of ion-cluster interactions in supersonic flows of hydrocarbons opens up the possibility of their use in GTL technology.

The work is performed with the financial support of the grant from the Russian government No. *11.G34.31.0046* for public support of scientific research under the guidance of leading scholars in Russian universities (leading scientist - K.Hanyalich, NSU).and by the Ministry of Education and Science of the Russia, project No. *3.749.2011*.

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COMPREHENSIVE CFD MODEL OF REACTOR FOR OXIDATIVE COUPLING OF METHANE

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Oxidative coupling of methane (OCM) to higher hydrocarbons is a potential route for direct conversion of methane to value-added products. Although the OCM process was discovered 30 years ago, it still has no practical implementation. On the stage of scaling-up it faces several difficulties such as high heat evolution, non-uniformity of temperature distribution, selectivity lost, catalyst deactivation. Reactor simulation could provide with a valuable information for a more rational process design.

The aim of this work is to develop a reliable quantitative model of OCM reactor that includes a description of flow field coupled with heat transfer as well as kinetic model. All simulations are done using open-source packages 'OpenFOAM' for the CFD calculations and 'Paraview' for the visualization of results. Simulations are carried out for a fixed bed tubular reactor loaded with granulated catalyst operating in a steady state regime. To describe gas flow in porous medium and mass transport in the reactor, the Ergun and the Navier–Stokes equations are used, respectively.

The kinetic description of the OCM process is based on the notion on its free-radical nature combined with the Mars-van Krevelen (redox) approach, assuming that the same oxidizing active sites participate in the formation of ethane from methane and ethylene from ethane. The values of kinetic parameters for model catalysts (PbO/Al_2O_3, $NaWMn/SiO_2$, Ln-Mg-oxides) are obtained in a quartz flow micro-reactor in differential regime. Composition, flow rate and temperature of the initial gas mixture, parameters of the catalyst (physical properties, particle size) and dimensions of the catalyst bed were the main variables. Thus, the effects of aerodynamic factors (uniformity of flow distribution, effect of 'inert' filling) and heat transfer (axial and radial) onto the efficiency of target product (ethylene) formation is analyzed.

The validity of the reactor model is verified based on the experimental data obtained in an enlarged flow reactor charged with up to 100 ml of catalyst.

KINETICS OF OXIDATION OF BUTENE-1 TO METHYLETHYLKETONE IN THE PRESENCE OF A HOMOGENEOUS CATALYST (COMPLEX OF PALLADIUM + Mo-V-P HETEROPOLY ACID)

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Methylethylketone (butanone, MEK) is the universal solvent widely used in many industries. Now it is produced by 3-stage technology, which is processed butylene fraction (by-product of 1,3-butadiene). We suggested a method of direct catalytic oxidation of *n*-butenes with dioxygen to MEK via reaction (1) [1].

$$n\text{-}C_4H_8 + {}^1/_2\, O_2 \xrightarrow{Pd+HPA-x} CH_3COC_2H_5 \qquad (1)$$

Aqueous solutions containing Pd(II) complex and Keggin-type Mo-V-P heteropoly acids $H_{3+x}PV_xMo_{12-x}O_{40}$ (HPA-x, x = 2-6) were used as catalysts for this process. Since the reduced forms of HPA-x (H_mHPA-x) are able to be oxidized with O_2, therefore in the MEK-process HPA-x is a *reversible* oxidant.

The stepwise reaction (1) is performed via two stages (2) and (3) which are accomplished in *two* different reactors. Such two-staged method permits to obtain high selectivity in reaction (2) and exclude a direct contact between n-C_4H_8 and O_2.

$${}^m/_2\; n\text{-}C_4H_8 + \text{HPA-x} + {}^m/_2\, H_2O \xrightarrow{Pd^{2+}} {}^m/_2\, CH_3COC_2H_5 + H_m\text{HPA-x} \qquad (2)$$

$$H_m\text{HPA-x} + {}^m/_4\, O_2 \longrightarrow \text{HPA-x} + {}^m/_2\, H_2O \qquad (3)$$

After reaction (2), flowing at 50-60°C in the ***reactor 1***, butanone is distilled off from the reduced catalyst, which is then regenerated in the ***reactor 2*** (T>100°C, P_{O_2}=2-4 at) via reaction (3). The kinetics of reaction (3) was reported in our work [2].

In the present work, the kinetics of reaction (2) in the presence of HPA-x (x=1-4) is studied. The catalytic reaction (2) consists of two stages, (4) and (5):

$$n\text{-}C_4H_8 + Pd^{2+} + H_2O \longrightarrow CH_3COC_2H_5 + Pd^0 + 2\,H^+ \qquad (4)$$

$$\text{HPA-x} + {}^m/_2\, Pd^0 + m\,H^+ \longrightarrow H_m\text{HPA-x} + {}^m/_2\, Pd^{2+} \qquad (5)$$

The redox potential, *E*, of the HPA-x solution decreases during the reaction (2). When *E*(HPA-x/H_mHPA-x) becomes equal to *E*(Pd_{ox}/Pd_{red}), the rate of reaction (2), W_2, falls down to zero. This occurs at almost complete reduction of V(V) to V(IV).

Dependencies $V_{C_4H_8} = f(\tau)$ have an initial linear part with a constant rate W_2 for all HPA-x. During the linear parts of the kinetic curves, the *E* values are over 0.76 V. At the lower HPA-x concentrations, the linear parts become shorter without a change of the initial rates W_2.

It was found that the kinetics of oxidation of butene-1 to butanone in the presence of homogeneous catalysts (Pd + HPA-x, $1 \leq \mathbf{x} \leq 4$) does not depend on the number of vanadium atoms **x** in HPA-x.

Reaction (2) appears to be of the 1st order with respect to C_4H_8, and of the ~0.64th order with respect to Pd. Such order may be explained by the existence of at least two active complexes of reduced palladium, which are in equilibrium (6) with each other:

$$Pd^0 + Pd^{2+} \longleftrightarrow Pd_2^{2+} \qquad (6)$$

The reaction rate does not depend on the concentration of HPA-x and the acidity of the catalyst solution (in the range of $0.16\ M \leq [H^+] \leq 2.2\ M$). It follows that HPA-x forms a complex with reduced Pd atoms. Its decomposition is the rate-controlling step in the reaction (2). In such case, the stages (4) and (5) may be presented by equations (4a) and (5a):

$$n\text{-}C_4H_8 + Pd_2^{2+} + H_2O \longrightarrow CH_3COC_2H_5 + 2\ Pd^0 + 2\ H^+ \qquad (4a)$$

$$2\ Pd^0 + \text{HPA-x} + 2\ H^+ \longleftrightarrow [Pd^0 (\text{HPA-x})\ Pd^0] \longrightarrow Pd_2^{2+} + H_2\text{HPA-x} \qquad (5a)$$

The apparent activation energy, E_a, proved to be variable. It decreases gradually when the temperature increases. So, for all HPA-x (x=1-4), E_a equals (58±5) $kJ \cdot mol^{-1}$ in the temperature interval 30-40°C, and (10±3) $kJ \cdot mol^{-1}$ at 60-70°C. The complicated temperature dependencies do not permit us to describe the kinetics of the reaction (2) by a single equation for a wide temperature interval. However, an approximate equality of W_2 for all HPA-x and the analogy of the kinetic dependencies allow us to give the empirical equation (7):

$$W_2 = k_2 \cdot [Pd]^{0.64} \cdot [C_4H_8] \cdot [\text{HPA-x}]^0 \qquad (7)$$

It is true for the (Pd + HPA-x) solutions at 30-70°C and $E(\text{HPA-x} / H_m\text{HPA-x}) > 0.76$ V. The k_2 value is ca. $5.7 \cdot 10^3 \cdot L^{0.64} \cdot mol^{-0.64} \cdot min^{-1}$ at 60°C.

This equation was used in the calculation of the ***reactor 1*** for the pilot plant.

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THE PROS AND CONS OF DMDS REPLACEMENT WITH H_2S IN AN OLEFIN PLANT

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Abstract

In the present paper, the feasibility of replacing DMDS with H_2S offgas has been investigated from the industrial viewpoints in the steam cracking of gaseous feedstocks. The purpose of this study is to evaluate the possibility of replacing DMDS, with an environmentally pollutant H_2S offgas sent to flare in aromatic plants. The effect of hydrogen sulfide (H_2S) and dimethyl disulphide (DMDS) on the rate of coke deposition and CO formation are compared over Incoloy 600, and stainless steel, individually in the lab scale.

Introduction

In industrial olefin plants, additives are commonly used to control CO production, and inhibit coke formation. Thus, different types of anti-coking chemical additives are employed commercially and/or under study, i.e. sulphur containing compounds, such as dimethyl sulphide (DMS), dimethyl disulphide (DMDS), hydrogen sulphide (H_2S); organo-phosphorus chemicals [1-2]; sulphur-silicon additive liquids [3-4]; and tin-based (tin/silicon mixtures, etc.) [5] additives [6]. The most prevalent conventional approach to coke suppression in cracking process is the intentional addition of sulfur compounds, i.e., dimethyl sulphide (DMS) or DMDS to the feedstock [4, 6-7]. The most abundant sulfur-containing species produced via thermal decomposition of DMDS is H_2S; consequently, the formed H_2S plays the principal coke inhibiting function [7-8]. The appropriate substitution of DMDS with the H_2S offgas not only provides a very low-priced supply for replacement with DMDS in olefin plants (abundant sources of pollutant H_2S offgas streams), but also restrain emitting the poisonous H_2S offgas to the environment. Furthermore, The influence of H_2S on coke deposition and CO_2 formation in the steam cracking of LPG as an industrial feedstock is investigated for the first time over Incoloy 600 and stainless steel, individually.

Results and discussion

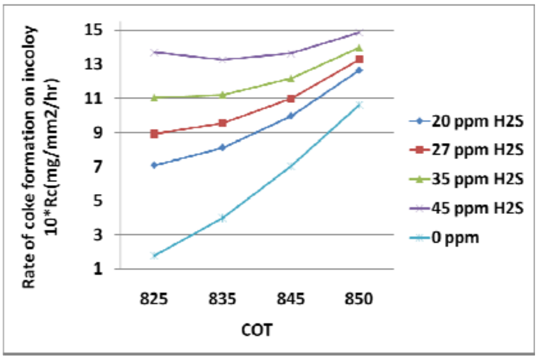

Figure 1. The effect of temperature on the rate of coke formation over Incoloy at various H_2S concentrations

At first, the limitations of the steam cracking process, such as the presence of impurities and contaminants in H_2S offgas, the appropriate injection point, and the safety necessities are evaluated in the prsent research. The experiments were performed in a laboratory unit consisting of five main sections, i.e. the feeding, the preheater, the furnace and reactor, the cooling, and the analysis.

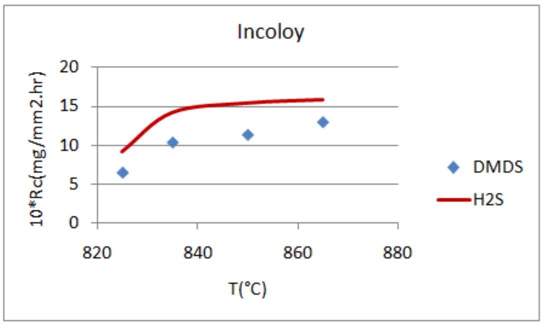

Figure 2. The influence of DMDS on the rate of coke formation over Incoloy compared to H_2S

The rate of coke deposition is increased over both of the elements by enhancing the reaction temperature because of the endothermic nature of steam cracking reaction. The experimental results depicted that the overall rate of created coke over Incoloy coupons is higher than stainless steel in all the experiments conducted at the same operating condition. Furthermore, it was observed that the rate of coke formation is elevated by increasing the concentration of H_2S. The yield of CO is decreased by enhancing the concentration of H_2S in the reaction medium. The rate of coke formation in the presence of DMDS is less than that when it is substituted with H_2S.

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KINETICS OF 2-METHYLBUTENE-2 EPOXIDATION WITH 2-METHYLBUTANE HYDROPEROXIDE

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The kinetics of 2-methylbutene-2 epoxidation with 2-methylbutane hydroperoxide was studied in the presence of a molybdenum catalyst. The analysis of the rate curves for the reaction showed that this reaction follows the general trends characteristic of the hydroperoxide epoxidation of olefins. The rapidly formed catalytic complex of HPMB with the catalyst interacts with OL to give OMB and the corresponding alcohol. The alcohol also forms a complex with the catalyst, inhibiting the entire epoxidation process. The distinctive feature of this process is the fact that the latter equilibrium resulting in the simple inhibition of the reaction by the products shifts to the left with an increase in the olefin concentration in the solution. As a result, the reaction rate changes out of proportion to the olefin concentration, although the first order of the reaction in the olefin is clearly observed in the initial portion of the rate curves. The phenomenon of the unusual effect of the olefin accounts for the enhanced stability of the molybdenum compounds in the presence of olefins and, in some cases, the catalyst activation. This phenomenon is likely due to the so-called steric factor, because the reactants possess bulky substituents, and is not observed for simple olefins. The revealed features of the process and its mathematical description make it possible to more competently design a reactor unit for the commercial production of isoprene according to the developed scheme. The main kinetic constants were calculated.

PP-I-12

PYROLYSIS OF POLYETHYLENE OVER ALUMINA INCORPORATED MCM-41 CATALYST

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Plastic materials are widely used throughout the world due to their low price, high capacity of production and simple processing techniques. An increase in their consumption causes a rapid accumulation in the amount of plastic wastes and critical environmental problems. Most of them are non-biodegradable. Landfilling, incineration and mechanical recycling methods for disposal of these plastic wastes have been used. However, the available space for landfilling process is decreasing day by day, whereas incineration is considered to be dangerous due to probable emission of toxic chemicals, mainly polychlorinated aromatic species. Therefore, chemical recycling of plastic wastes is regarded currently as a promising alternative. They are degraded into lower molecular weight liquid and gaseous products which are potential raw materials and fuels for petrochemical industry. The use of catalysts enhances the formation of more valuable hydrocarbons at lower reaction temperatures and residence times. In catalytic pyrolysis, zeolites, clays and mesoporous materials can be used as catalysts [1-3].

In this study, alumina loaded MCM-41 catalysts were synthesized in order to be tested in the pyrolysis of polyethylene. The pure MCM-41 catalyst was synthesized using hydrothermal synthesis route and the alumina containing ones with different Al/Si ratios were synthesized using an impregnation method [1, 2]. These synthesized materials had high surface areas in the range of 967-1262 m^2/g and exhibited isotherms of Type IV. ^{27}Al NMR spectra of the catalysts exhibited tetrahedrally and octahedrally coordinated aluminum species in the structure. TEM images showed well-ordered hexagonal arrays of uniform mesopores with channels.

After the characterization of these catalysts, their performances have been investigated in the polyethylene degradation reaction using a thermal analyzer. The analysis was performed under nitrogen atmosphere at a flow rate of 60 cc/min, in a temperature range of 30-550°C with a heating rate of 5°C/min. The TGA results showed a remarkable decrease in the decomposition temperature of polyethylene, as shown in Figure 1. A standard power law model was used to describe the kinetics of polyethylene degradation reaction. The overall order of the polyethylene degradation was found to be 1. The activation energy of the polyethylene degradation reaction in the absence of catalyst was found to be 136 kJ/mol. The activation energy remained almost constant in the presence of the catalysts with higher Al/Si ratios. A reduction in the activation energy of the reaction in the presence of catalyst was not observed. However, in the presence of the Al-0.03 catalyst, it was found to be 106 kJ/mol.

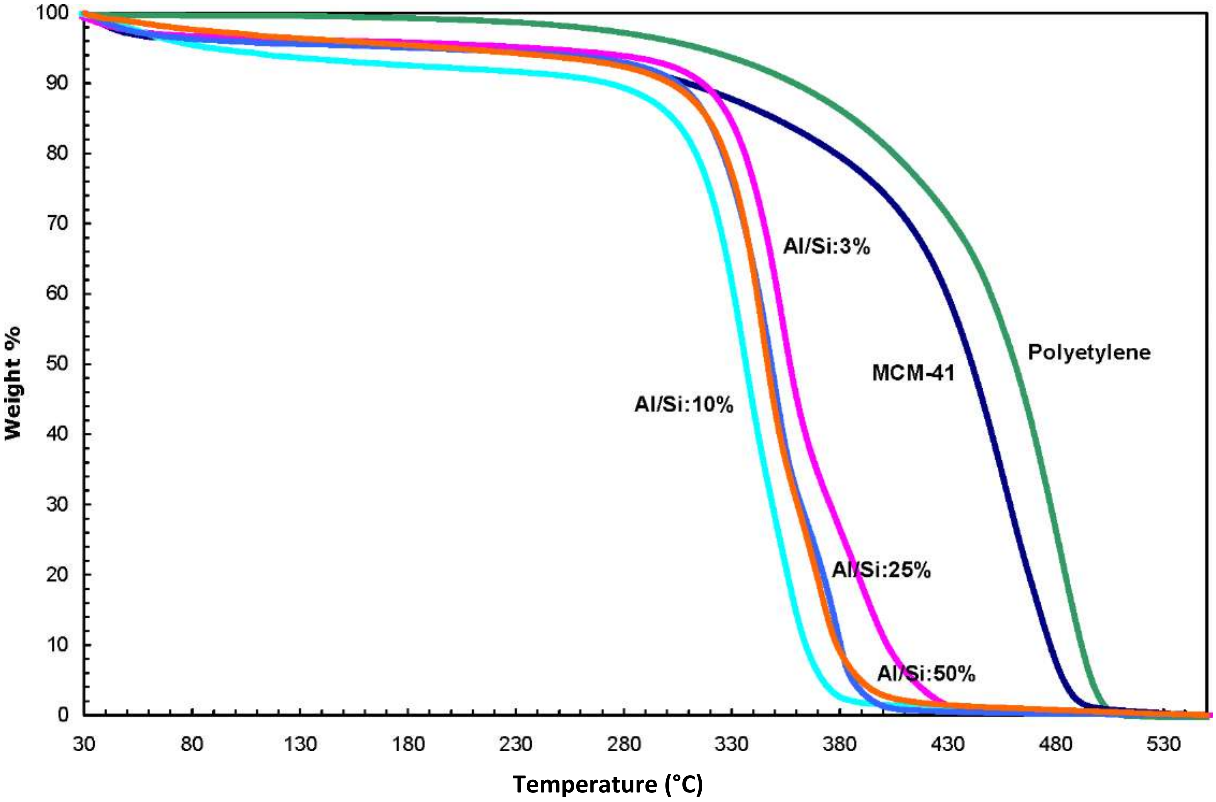

Figure 1. TGA plot describing the pyrolysis of polyethylene over pure and alumina loaded MCM-41 catalysts.

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PP-I-13

KINETIC EVIDENCE FOR EQUILIBRIUM BETWEEN PROPYLENE GLYCOL AND HYDROXYACETONE DURING BUTYL LACTATE HYDROGENOLYSIS

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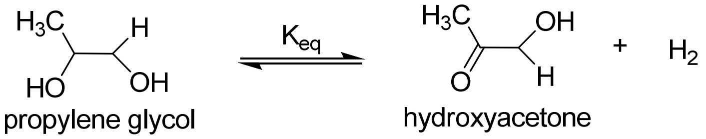
Nowadays design of the new catalytic routes starting from platform bio-derived molecules derived from renewables and different from the traditional chemical synthesis routes starting from fossil fuels is one of the key issues of sustainable development [1] Thus, commercial production of propylene glycol widely used as a solvent or a reagent in pharmaceutical and chemical industries is currently petroleum-based and involves high pressure and high temperature hydrolysis of propylene oxide produced by either chlorohydrin process or the per-oxidation process which is unfavorable from green chemistry viewpoint. A catalytic method starting from lactic acid obtained by fermentation of crude biomass provides an eco-friendly alternative to the petroleum-based process for 1,2-propanediol synthesis. To perform the hydrogenation process more effectively lactic acid is usually converted into more readily reducible esters, such methyl- [2], ethyl- [3] or butyl lactate [2]. However it is very little data about byproducts formation in spite of importance of such information for reaction network evaluation. So, the main idea of current work is to provide new insight into reaction understanding by kinetics investigation.

The experiments on hydrogenolysis of lactic acid esters were carried out in a vertical U-shaped flow reactor under hydrogen flow (10 Lh^{-1}) at atmospheric pressure in a temperature range of 433 ÷ 493 K. The reactor represents a quartz tube loaded with 45,5 wt.% Cu/SiO_2 catalyst grains (0.5 g, 0.25÷0.5 mm) diluted by an inert quartz beads (3 g, 0.63÷1.6 mm) equipped with a thermocouple and heated by a furnace. Neat butyl lactate was fed into the reactor using a syringe pump, vaporized in the preheated line and mixed with purified hydrogen, thereafter the vapour mixture passed through the catalyst bed. The volatile products were collected in a downstream trap with liquid nitrogen and analyzed by GLC, GC/MS and ^1H NMR.

The main byproduct of the reaction was observed to be hydroxyacetone. Formation of hydroxyacetone can be considered as a side reaction of propylene glycol dehydrogenation over metallic copper particles. However, it was found that the ratio of products is changed depending on temperature but is independent on residence time. Thus one can suggest that the equilibrium between propylene glycol and hydroxyacetone (1) is achieved:



(1)

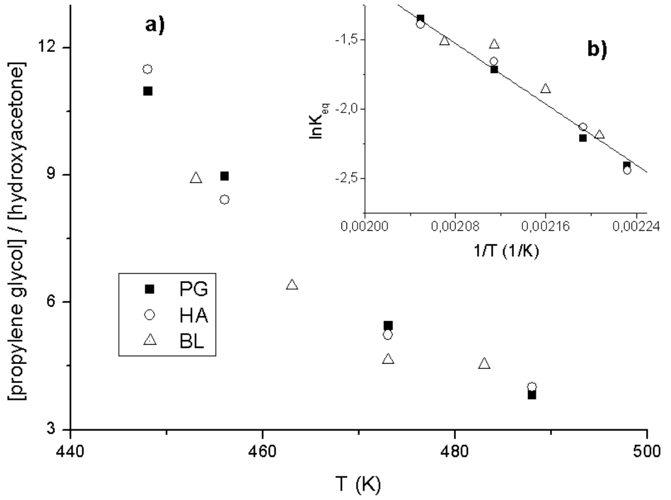


Figure 1. Ratio of propylene glycol to hydroxyacetone vs. temperature (a) and temperature dependence of equilibrium constant K_{eq} (b) in propylene glycol dehydrogenation (PG), hydroxyacetone hydrogenation (HA) and butyl lactate hydrogenolysis (BL) over 45.5% Cu/SiO_2, substrate / H_2 = 1:70 (molar ratio).

To confirm this hypothesis the reaction was commenced from the products - propylene glycol and hydroxyacetone. Dehydrogenation of neat propylene glycol as well as hydrogenation of neat hydroxyacetone was performed in hydrogen atmosphere at the same temperature as butyl lactate hydrogenolysis. As demonstrated on Figure 1b, hydroxyacetone formation was observed from propylene glycol even in an excess of hydrogen, moreover propylene glycol was formed from hydroxyacetone. The ratio between propylene glycol and hydroxyacetone both in the forward (propylene glycol dehydrogenation) and in the backward reactions (hydroxyacetone hydrogenation) was inversely changed with reaction temperature. It means that hydrogenolysis mechanism apparently involves the equilibrium between propylene glycol and hydroxyacetone. This equilibrium seems to be controlled by hydrogen partial pressure.

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KINETICS OF D-GLUCOSE HYDROGENATION OVER POLYMER-BASED RUTHENIUM CATALYSTS

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Selective hydrogenation of monosaccharides (i.e. D-glucose) to corresponding polyatomic alcohols is industrially important reaction. Hydrogenation product (sorbitol) is widely used in various industries (it is an excellent humectant and texturizing agent, and also used in production of pharmaceuticals, cosmetics and vitamin C), but their major application is sugar replacement [1, 2].

The most well-known catalyst of the saccharide hydrogenation is Ni-Raney. However, it has several drawbacks: formation of side-products, pollution of the target product with Ni^{2+} ions, deactivation of catalyst with time; necessity to use modifiers (B, Cr, Mo, Sn, Fe, P) to increase catalytic activity [3-6]. Ru-containing catalysts are promising alternative to Ni ones, as Ru reveals no leaching, no catalyst deactivation, and high activity (in 50 times higher than Ni) [7, 8] However, the key factor in the case of Ru-based catalysts is the choice of support. Carbonic supports (e.g. carbon nanotubes, graphenes, activated carbon, etc.) are most preferable due to the following reasons: (i) in comparison with inorganic oxides (e.g. TiO_2, Al_2O_3, SiO_2) carbonic supports are more stable in low acid and chelating reaction medium; (ii) Ru is more active and stable due to the electron donation from Ru to the carbonic support; (iii) unique contact between Ru and carbon support favors hydrogen spillover [2, 6, 7, 9, 10]. Thus we propose polymeric support of hypercrosslinked polystyrene (HPS) to be promising for D-glucose hydrogenation process.

In this work 3%-Ru/HPS catalysts were synthesized and tested in selective hydrogenation of D-glucose to sorbitol at variation of reduction method, reaction temperature, hydrogen pressure and D-glucose loading. Physicochemical investigation of Ru/HPS catalysts was provided via TEM, SEM, XPS, XRD and element analysis. Figure 1 presents TEM image of HPS-stabilized Ru nanoparticles (mean diameter of nanoparticles in all the samples doesn't exceed 1.4 nm).

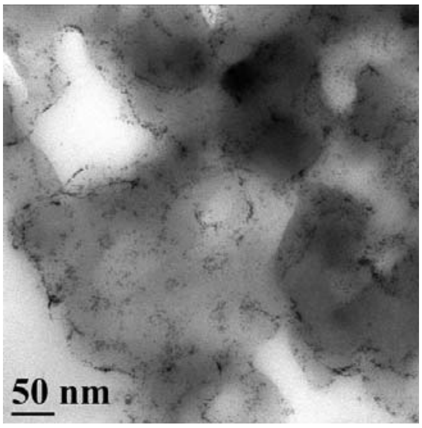

Fig. 1. TEM image of HPS-stabilized Ru nanoparticles

It is noteworthy that synthesized catalysts revealed high activity and selectivity (higher than 98%) in D-glucose hydrogenation to sorbitol.

As a result of kinetic and physicochemical investigations we proposed the existence of two active sites on the catalyst surface (Ru (0) and Ru (IV), according to the XPS data) and hence uncompetitive sorption of hydrogen and D-glucose.

Besides, kinetic investigation allowed us to put forward the hypothesis on hydrogenation mechanism. We proposed the existence of two subsequent stages of D-glucose hydrogenation with different rate constants (Figure 2):

(i) “fast” stage corresponding to the non-stationary processes, which are due to the catalyst pretreatment procedure;

(ii) “slow” stage of common stationary hydrogenation.

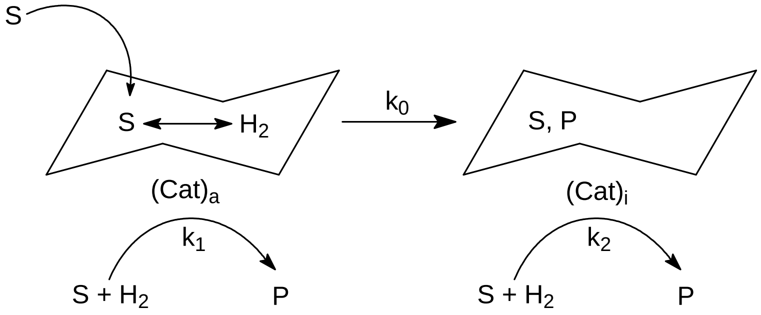

Fig. 2. Scheme of D-glucose hydrogenation

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PP-I-15

CFD ANALYSIS OF HEAT LOSSES FROM A MICROREACTOR FOR THE STEAM REFORMING OF METHANOL

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Introduction

The steam reforming of methanol (SRM) in catalytic microreactors is interesting for the production of H_2 for onboard and portable applications of fuel cells. The high surface-to-volume ratio characteristic of microreactors enhances the mass and heat transfer rates, produces very low pressure drop and allows easy thermal integration of the processes involved. In this communication we report on a computational fluid dynamics (CFD) study of the heat losses from a catalytic microreactor for the SRM reaction, which is an important aspect of the microreactors operation that has not received much attention so far.

Results and discussion

In this work we study the non-isothermal SRM with a fixed H_2O/methanol molar ratio of 1.25 in a microreactor with a thin layer (4 mg/cm^2) of a 2.5 wt. % Pd on ZnO catalyst uniformly deposited onto the inner walls of square microchannels of 0.7 mm of side and 20 mm of length. The reaction scheme included the SRM, reverse-WGS and methanol decomposition reactions. The rate equations of these reactions over the Pd/ZnO catalyst were established in a previous study, and have been implemented in the CFD simulation code. The physical model of the microreactor consisted of a steel block containig 100 square parallel microchannels (Figure 1A) which is heated at 6 points emulating the presence of electric cartridges. This block is fed through a flow distribution chamber. Several designs of this chamber have been considered varying its dimensions, as shown in Figure 1B. We have also studied a microreactor equiped with 10 microslits of 0.7 mm x 13.3 mm x 20 mm. The heat input (Q) is set according to: Q = *methanol molar feed flow-rate* x ΔH_{SRM} x F_Q, where ΔH_{SRM} is the SRM heat of reaction and F_Q is a parameter that

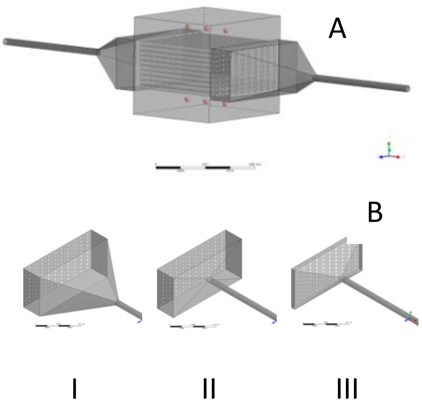

Figure 1. Physical models

has been introduced to model the additional energy that is necessary to heat the feed stream up to the reaction temperature, to compensate the heat consummed by the decomposition reaction and finally to compensate the heat losses. To investigate the influence of heat losses, we have considered different values of the convection heat transfer coefficient (h = 0, 5 and 10 W/m^2°C) and a constant mean external temperature of 30°C.

Regarding the effect of the flow distribution chambers design, it has been found that only at high space velocities (> 20,000 h^{-1}) there is a significant effect on the gas distribution into the microchannels. However, the mean methanol conversion at the microreactor exit remains almost unchanged due to a compensation between the performance of the channels with higher and lower residence times.

Figure 2 shows the mean methanol conversion at the microreactor exit achieved for different values of the parameter F_Q and chamber type I (Fig. 1). In absence of heat losses (h = 0) it can be seen that the energy required to achieve complete SRM conversion is about 2-2.5 times the heat of the SRM reaction. This greater energy requirement is due to the combined effect of the sensible heat of the feed stream and the methanol decomposition reaction. In the presence of heat losses by convection these requirements are substantially increased, specially for the lower space velocities that may even require between 5 and 10 times the amount of heat required by the steam reforming reaction. Clear temperature profiles are observed in the chambers, especially for high convective losses, but the microreactor block is nearly isothermal (430°C). As concerns the microreactor based on microslits, there is a greater influence of the heat losses compared to the square microchannels. Higher values of the F_Q parameter are required to achieve the same methanol conversion.

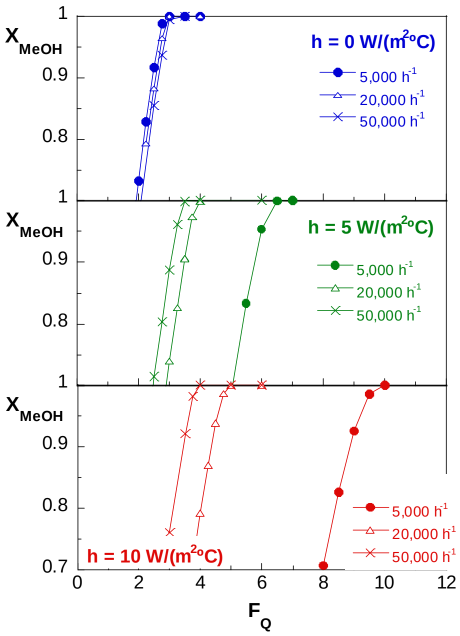

Figure 2. Effect of the heat losses on the SRM conversion

Acknowledgements

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PP-I-16

PRESSURE DROP OF STRUCTURED CARTRIDGES WITH FIBER-GLASS CATALYSTS

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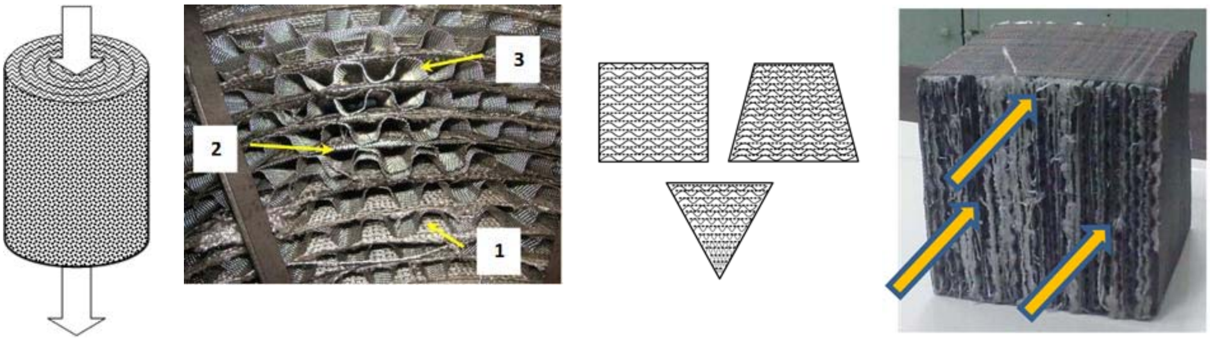
Novel catalysts comprising noble metals (Pt and Pd), supported on fiber-glass woven support [1] has attained a lot of attention recently both from theoretical and applied points of view. The research investigations [2] showed that such catalysts demonstrate unique catalytic properties and may be used for performance of a wide range of catalytic reactions. Moreover, specific heat/mass transfer properties [3], original geometry, high flexibility and high mechanical strength of such catalysts give the way to develop really new catalytic processes and novel reactor designs.

Recently, the various structured cartridges were proposed for packing of the glass-fiber catalyst (GFC) fabric were proposed [4,5] (fig. 1). Such cartridges are convenient for construction of catalyst beds of any size and geometry.



(a) (b)

Fig.1. Spiral (a) and prismatic (b) GFC cartridges structured with corrugated metal gauze

This study was dedicated to investigation of the pressure drop of such cartridges. The experiments included measurement of the pressure drop under variation of the air flow rate for cartridges with variation of:

- external cartridge shape (spiral cylinder, square prism);
- the size of the channel for flow passage (in the range from 3 up to 10 mm);
- fiber-glass fabric structure (sateen and lightweight types);
- types of structuring elements (corrugated gauze with flat gauze, chain-link gauze with and without flat gauze).

It was shown (fig. 2) that:

- unit hydraulic resistance of cartridges significantly depends upon the size of the flow passages – increase of the distance between the GFC layers leads to decrease of hydraulic resistance;
- cartridge pressure drop practically does not depend upon the structure of the fabric and upon the external shape of the cartridge;
- pressure drop significantly decreases under the use of chain-link gauze instead of the corrugated gauze;
- exclusion of the flat structuring gauzes from the cartridge design leads to much higher hydraulic resistance of the cartridge (resulting from decrease of the actual flow passages).

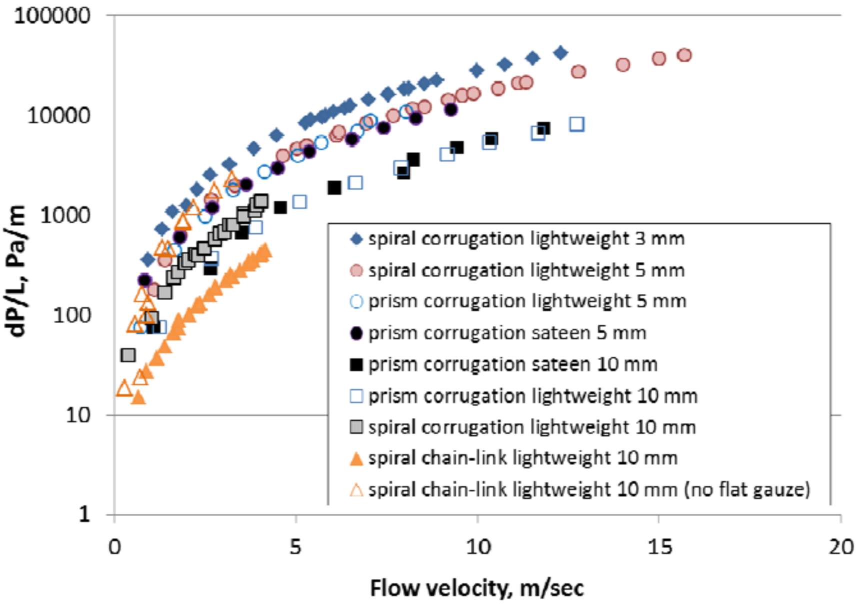


Fig.2. Unit pressure drop per unit cartridge length vs air flow (ambient pressure, 20°C) velocity for the GFC cartridges with gliding flow.

The equation for engineering calculation of the pressure drop for GFC cartridges with various geometry was proposed.

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POSTER PRESENTATIONS

SECTION II

Chemical Reaction Engineering and Reactors Design – Novel Approaches, Modeling, Scale-Up, Optimization

VALORISATION OF CO_2 IN A FILTER-PRESS ELECTROCHEMICAL REACTOR: MODELLING THE INFLUENCE OF FLOW CONDITIONS ON FORMATE FORMATION

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Several options to reduce the atmospheric concentration of carbon dioxide (CO_2) and mitigate climate change are being considered. Among the different alternatives to tackle this problem, valorisation of captured CO_2 appears as a more interesting option than carbon storage, since it allows the recycling of CO_2 into added-value products. Particularly, electrochemical reduction has been pointed out as a promising method for CO_2 valorisation and its conversion into industrially useful chemicals [1], such as formate, which is a chemical used in pharmaceutical syntheses, paper and pulp production with a growing demand. Different recent studies (e.g. [2-4]) have paid particular attention to the direct CO_2 electroreduction to formate, which reflects the increasing interest in this type of valorisation approach.

This work focusses on analysing and modelling the influence of catholyte flow rate in the performance of an experimental system for continuous CO_2 electrochemical reduction to formate at ambient temperature and pressure conditions. A filter-press type reactor, with a Nafion cation-exchange membrane that separated the anodic and cationic compartments, was used. A lead plate with a surface area of 10 cm^2 was the working electrode, while a DSA plate was the counter-electrode. An aqueous solution 0.45M $KHCO_3$ + 0.5M KCl, which was maintained saturated with CO_2 using constant bubbling throughout the experiment, was used as catholyte, and 1M KOH was used as anolyte.

Experiments were carried out at different electrolyte flow/ area (Q/A) ratios within the range of 0.57 and 2.3 mL min^{-1} cm^{-2}, using a constant current density of 12.25 mA cm^{-2}. The results obtained indicated that in the studied electrochemical system increasing the catholyte flow to overcome mass transport limitations only had beneficial effects for the lowest flow/area ratios; at Q/A higher than 0.76 mL min^{-1} cm^{-2}, increasing the catholyte flow rate did not result in better performance of the process, which could suggest that in such conditions the electrochemical reaction of formate formation may be limited by other aspects, such as adsorption equilibria in the surface of the working electrode. The influence of these aspects had also to be taken into account by including correction factors in a simple model proposed to relate the production of formate to flow conditions and geometric variables in the filter-press cell. Based on the model developed by Pickett [5] to relate conversion per pass in a parallel-plate electrochemical reactor with their geometric variables and flow conditions (Reynolds number), the following expression was proposed:

$$c_{formate} = c_i \left[1 - exp\left\{-2.33\left(\frac{D_R\, L}{Re\ v\ S}\right)^{2/3}\right\}\right] \quad \text{[Eq. 1]}$$

where $c_{formate}$ is the measured concentration of formate produced and c_i represents the initial concentration of CO_2 reactant that is actually available to react. However, fitting the formate concentrations obtained using different Q/A ratios (i.e. different Re) to Eq. 1 only gave R^2=0.9065. Considering the reaction mechanism of CO_2 electro-reduction proposed by different authors [e.g. 6, 7], which involves the adsorption of CO_2 on the surface of the cathode electrode and the formation of the intermediate radical $\cdot CO_2^-$(ad) that after winning a proton and another electron finally yields formate, Eq. 1 was modified with a correction factor to include the possible influence of adsorption equilibria in the cathode surface. The improvement of R^2 (0.9603) when fitting the experimental data suggested the applicability of this simple model, although further research is needed to ascertain the detailed mechanisms that regulate the reduction of CO_2 to formate in this continuous electrochemical process.

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Acknowledgements

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REACTOR FOR PURIFICATION AND COOLING THE EXHAUST GASES FROM THE STATIONARY DIESEL ENGINES

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Purification and cooling the exhaust gases from the stationary diesel engines in the emergency systems for electricity supply is an important environmental task. The current work was devoted to development of the reactor for solution of this problem.

The proposed reactor (Fig. 1) comprises the catalytic neutralizer for oxidation of CO and hydrocarbons and vortex scrubber for cooling of the exhaust gas and absorption of NOx, SO_2 and soot particles by water.

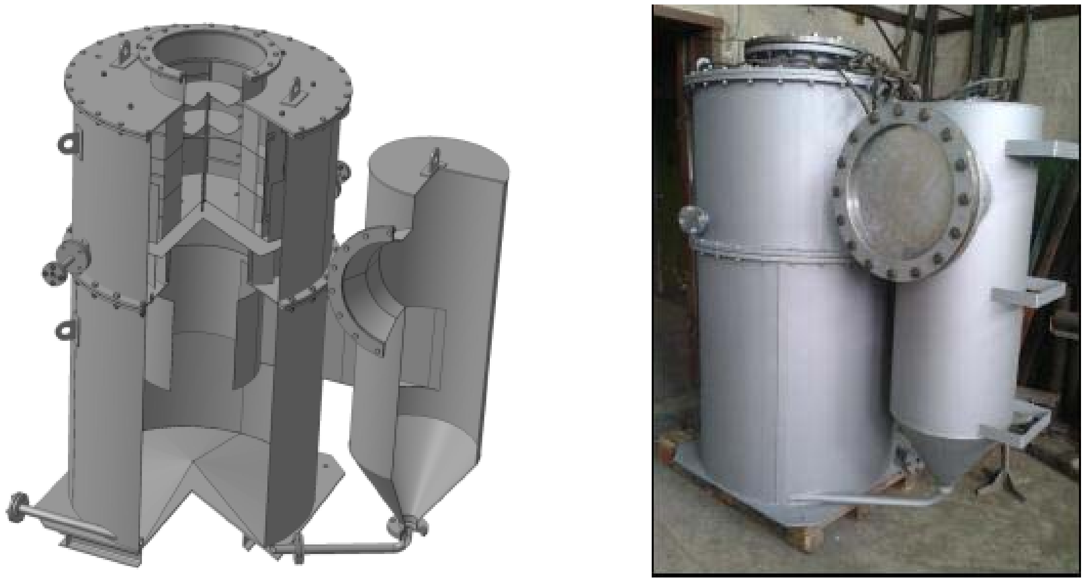

Fig. 1. Internal design (left) and external view (right) of the reactor for purification and cooling the ehaust gases from 630 kW diesel engine.

The catalytic neutralizer is made on the base of the radial catalyst bed, with Pt supported on fiber-glass woven support [1] as a catalyst. The catalyst clothes were structured by layers of flat and corrugated metal gauze in form of cubic cartridges [2] (fig. 2). Such cartridges are characterized with low pressure drop and high robustness in presence of soot particulates, moreover they are very mechanically stable under significant vibration, which is typical for large-scale diesel engines.

Fig. 2. External view of the catalytic cartridge with glass-fiber catalyst.

Application of the vortex scrubber provides formation of the water-gas bubbling layer (fig. 3) with extremely high inter-phase exchange area and, therefore, with high intensity of the gas cooling and removal of NOx/SO_2.

Fig. 3. Water-air vortex layer.

The proposed reactor design provides high purification and cooling efficiency in combination with quite moderate pressure drop (below 2.5 kPa) under nominal gas loading of ~3000 st.m^3/h typical for the exhausts from the 630kW diesel electricity generator.

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MULTIFUNCTIONAL CHEMICAL REACTOR FOR SMALL-SCALE PRODUCTIONS

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At the present time in world practice much attention is paid to the development of combined multi-functional reactors, which could simultaneously or consequentially carry out various processes. At the XIX International Conference on Chemical Reactors "CHEMICAL REACTOR-19" the vibrational multi-reactor, developed at the Institute, was presented [1]. It allows to conduct almost all chemical engineering processes, namely: dissolution, synthesis, crystallization, filtration, washing, distillation, conductive drying, crushing, extraction, adsorption-contact drying, catalytic processes etc. in one reacting volume, in any sequence, without depressurization and contact to environment.

The exception is the obtaining and processing of fine dispersed materials, for example: montmorillonite. To obtain this substance in the multifunctional vibrational chemical reactor was impossible because of the specific features caused by this dispersity of the material.

At present there is no equipment that meets and takes into account the specific characteristics of fine dispersed materials. Of particular difficulty are the processes of drying, filtration, grinding, fractionating. The drying process of these materials, having a pasty structure, is inextricably, linked with the formation of "cakes", requires additional grinding of the final product after drying, and hardware design practically excludes possibility of using a gas heat-carrier, requires intensive mixing, vacuum pumping.

A complexity of the filtering of fine materials is that they almost always form compressible precipitates, and this leads to increasing hydraulic resistance, reducing the rate of filtration, the formation of packed bed of precipitate extremely low-tech for the subsequent drying. The grinding process can be carried out only in the liquid phase. Consequently, all of the filtering and drying difficulties arise again.

Purpose of this work was to develop new hardware and technology solution of production and processing of fine materials. We have developed the fundamentally new fractional method of suspensions separation. The essence of the method is that the polydisperse suspension is fed to a set of filter partitions. They are arranged with a gap of one above the other in descending order of size of cells. The filter partitions are vibrating. The number of filters and cells size of each is determined by dispersivity of solid particles of suspension. Detained by each filter the particles of the solid phase under vibration is continuously removing from zone feed of suspension, without forming precipitate there. They do not hinder the free flow of the liquid phase with the smaller solid particles. Layer of precipitate at each of the filters is formed only at the exit from the zone feed of suspension and under vibration is transported to an unloading nipple. Vibrational transportation and dehydratation of deposit, caused by vibration, take place simultaneously. The use of directed harmonic vibrations allows to provide the specified condition, i.e. we have a combination of a filtering process, fractionation and vibrational transportation of precipitate. To carry out the drying of wet fine-grained material having a paste-like structure, a conductive drying of material in fluidized-bed is combined with the process of vibrational grinding. To intensify the process of drying and grinding a number of pre-dried materials were introduced in the pasty product, thereby increasing the heat transfer surface.

Creation of such chemical reactor provides a qualitatively higher level of solving the problem of obtaining and purification of most products of chemical synthesis.

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A UNIVERSAL CLOSE COUPLED CATALYST WITH IMPROVED GAS DISTRIBUTION

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Development of automobile catalysts with a high thermal stability makes possible to place the catalyst in immediate proximity to an engine (close coupled catalyst, CCC) that shortens the cold start period. In Russia, CCC are used since 2005 in combination with AVTOVAZ 8- and 16-valves engines. The important task that is still to be solved is to keep the uniformity of the exhaust gas distribution and temperature field across the catalytic unit to increase the efficiency of operation and the service life of the catalyst. An additional requirement is a uniform washing of a λ-tester with gas flow taking off from each cylinders to provide a correct composition control of the fuel-air mixture. A simpliest way of solving these tasks is the combining of gas flows taking off from different cylinders with following passing of the confluent gas flow through a diffuser of a neutralizer bellmouth where the λ-tester is installed. However, this way forces to widen the spacing between the engine and catalyst that in turn decreases the gas temperature and increases the neutralizer dimensions.

The introduction of the gas flows from the cylinders directly to the bellmouth seems to be a more reasonable way. For the gas introduction system, the main idea is to use curved-axis coniform branches with an outlet to inled diameters ratio varying from 1.5 to 2.0. Flowing out of such a branch, the gas distributes more uniform across the front section of the catalytic unit. In addition, when gas runs along such the branch, the flow rate decreases that reduces the pressure loss at the entrance into the bellmouth.

To receive the neutralizer both universal and manufacturable, that was made by traditional methods used for piped constructions: the housing consisted of two identical parts, the branches were produced from a ∅45 mm pipe by an original method of squeezing and bending. This construction can be installed on various 4-cylinder in-line engines with the swept volume of up to 2 l. A combination of two such constructions can be used for a double-row 8-cylinder engine. Several low-cost procedures were needed for the construction adaptation including changes of the length, tilt angle and squeezing ratio of the branches. In accordance with the swept volume, the length of the catalytic unit can be varied in the range of 125 mm maximum.

Table 1. The uniformity coefficients of the gas flow distribution

	16-valves engine	8-valves engine
Estimated along the area	0.97131	0.978701
Estimated by the mass consumption	0.971093	0.978586

Table 2. The uniformity of λ-tester washing

The cylinder's number	1	2	3	4
16-valves engine	1	0.96	1.09	0.92
8-valves engine	1	1.09	1.01	0.92

The practical tests was performed using the constructions adapted for AVTOVAZ 8- and 16-valves engines. The catalytic units tested in both cases were of 62 cm^{-2} (400 $inch^{-2}$) in channel density and 101.6 mm (4′′ inch) in length that corresponded to the active zone of the catalyst of 1.24 l.

The uniformity of the gas flow distribution was estimated by computational modeling The following characteristics of the exhaust gases were determined: the rate, temperature and pressure fields as well as the uniformity coefficient of the gas flow at the inlet of the catalytic unit (Table 1).

The uniformity of λ-tester washing with the gas flows was measured on a motor bench at idling regime. An additional specified flow of air was introduced in turn into the outlet branches of each cylinder controlling the oxygen concentration by the λ-tester. The value of the oxygen concentration after cylinder 1 was taken as a unit, and the concentrations after cylinders 2, 3 and 4 were given with respect to that for cylinder 1. These ratios were taken for the dergee of λ-tester washing uniformity with the gas flowing out of different cylinders (Table 2). To compensate high inaccuracy of this method, the oxygen concentration was measured for a long period of time (*ca*. 0.5 hr) with the following statistical treatment. As clear from Table 2, the relative nonuniformity of λ-tester washing did not exceed 10%.

Acknowledgements

The authors are grateful to the workers of OOO “Profil-VK” guided by V.D. Kal’ney and M.M. Rusakov for the studies performed by computational modeling.

EFFICIENCY INCREASING OF DEHYDROGENATION REACTOR BY WATER INJECTION OPTIMIZATION

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There are of lot of different ways for efficiency increasing of existing industrial plants. A well-known way to increase the efficiency of Paraffins Dehydrogenation industrial processes is a supply of water or water vapor into the reaction zone [1, 2].

Analysis of experimental data obtained at the industrial plant dehydration, showed that there is a dependence of the optimal amount of water the temperature [3]. Moreover, deviations from this optimal value, as in most, and in the down lead to a deterioration in the quality of the product.

It is known that in the dehydrogenation of higher alkanes, long chain hydrocarbons are involved, can tsiklizavatsya and polycondensed at temperatures of 450-490°C [4]. The formation of such products of hydrocarbons transformations leads to the formation of the primary coke structures on the platinum catalysts surface that block the active sites, which leads to the loss of its catalytic activity and reduce its service life. To prevent this process is fed into the reactor water dehydrogenation, capable of reacting with coke structures by oxidizing them, and forming a half-life of products [5].

Based on thermodynamic analysis and experimental investigation of catalysts has been proposed a method for determining the optimal dynamics of the water supply to the reactor, depending on the temperature of the process. The basis of the proposed method put the equation of equilibrium structures coke oxidation of water and the thermodynamic equation of change in the equilibrium constant of this reaction on the temperature.

The proposed method was tested on the installation of the olefins production. With the developed methodology, based on which was set up non-stationary mathematical model of the dehydrogenation of higher hydrocarbons C_9-C_{14}, were calculated the possible modes of water supply to the reactor and evaluated the effectiveness of the catalyst. The calculations showed that with increasing amounts of water supplied to the rise in temperature increases the life of the catalyst and the quality of the product (selectivity to mono-olefins) as compared to regular water supply in portions. Initially water supply into dehydrogenation was constant and low (Fig. 1), but it was later determined that increasing the water supply is effective to prolong the life time of catalyst and to have the operating temperature lower while keeping desired conversion level.

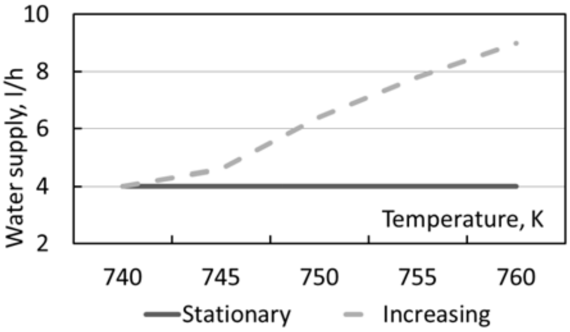

Figure 1. Stationary and increasing supplies of water.

The special software module allows calculating the amount of water to supply depending on operational conditions and production targets. Calculations showed that increased supply of water can make the life time of catalyst longer for up to 20% (Fig. 2).

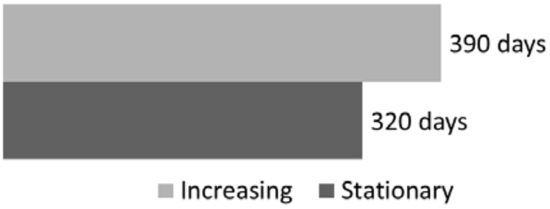

Figure 2. Dehydrogenation catalyst lifetime at stationary and increasing supplies of water.

Recommendations for water supply are implemented at the industrial plant, corresponding methods are protected by appropriate legal documents.

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Acknowledgements

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PP-II-6

USE OF MATHEMATICAL MODELING METHOD FOR REACTORS CONSTRUCTION OPTIMIZATION FOR NAPHTHA CATALYTIC REFORMING AND ISOMERIZATION PROCESSES

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The worldwide experience of petroleum refineries modernization shows, that almost all refineries to be modernize have the same set of well-known processes and technologies like desalting and preliminary distillation, hydrotreating of petrol and diesel fractions, light end isomerization and naphtha catalytic reforming. These units are often reconstructed during modernization, and in some cases new units are built in order to increase technicoeconomic and environmental characteristics of their operation. Mathematical modeling method allows estimating possible variants of oil-processing units reconstruction and choosing the optimal direction for further process upgrading.

Mathematical models for naphtha catalytic reforming and isomerization processes [1-4] were applied to calculation of different variants of feed input in radial flow reactors. The schematic presentation of radial flow reactor and possible variants of feed input are given in fig. 1.

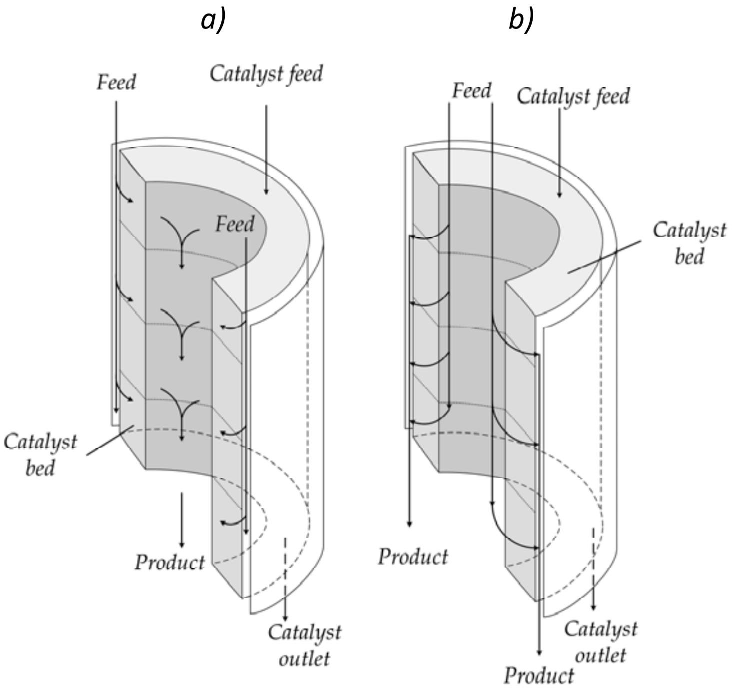

Fig. 1. Schematic representation of a radial moving-bed reactor for catalytic reforming

a) feed input from the reactor periphery

b) feed input from the reactor centre

Calculation shows that the input of feed into the central part of the reactor gives the considerable increase in product octane number both for naphtha catalytic reforming and isomerization processes (fig. 2) due to the higher conversion of hydrocarbons to valuable products.

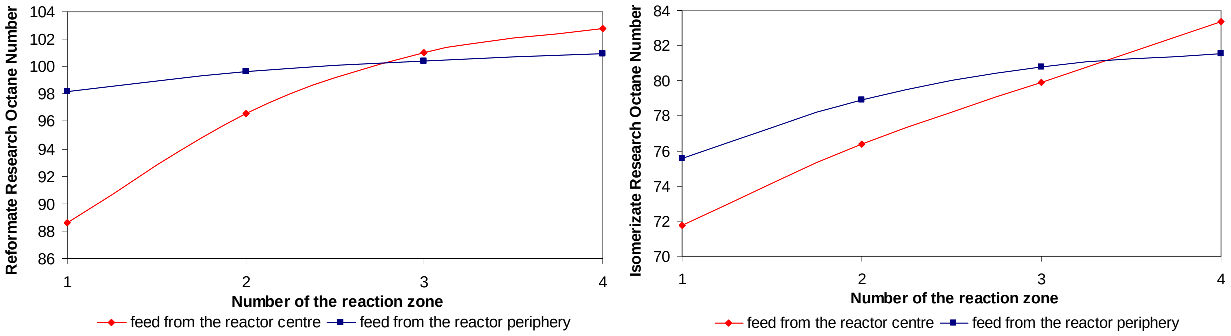

Fig. 2. Research octane numbers of reformate and isomerizate for different variants of feed input (simulation results)

Models calculations schow that the input of feed into the central part of the reactor leads to more uniform coking through the catalyst bed. This leads to the higher conversion of raw material to product. The reacting mixture velocity distribution, concentrations and temperature distributions are also more uniform in that case.

Using computer simulation it is also possible to compare the different units work efficiency and choose more suitable variant of process optimization for given raw material.

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EFFECT OF CATALYST MORPHOLOGY AND ACTIVITY IN THE PRODUCTION OF FUELS RANGE HYDROCARBONS

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Olefin oligomerisation is of importance to the petrochemical industry. Many olefin containing feeds like ethanol could be converted to gasoline range hydrocarbons and petrochemicals over a range of catalysts. The industrially preferred catalysts for this process are zeolite based catalyst. However, the activity of zeolite catalysts in many reactions is very much dependent on their acidity and pore sizes among other properties. While micro porous zeolites are known to favour the formation of gasoline range hydrocarbons; there is need to enhance pore control technologies in order to improve the production of diesel range hydrocarbons.

In this study we have investigated the selectivity of ZSM-5 type catalysts during the production of fuel range hydrocarbons; the product distribution is largely determined by catalyst acidity, particle size distribution and pore size.

The presentation focuses on explaining the correlation between the catalytic properties and the product distribution. The physical and chemical properties of the fresh and spent catalysts were determined using HRTEM, SEM, FTIR, ICPS, XRD and reactor studies. We have observed that tuning the catalyst activity by varying Si/Al ratio could change the product distribution; acidity and pore size structure are also attainable by desilication. However, much attention is needed to ensure that the ZSM-5 catalyst structure is not destroyed during desilication.

PP-II-8

PURIFICATION AND CONCENTRATION OF PECTIN POLYSACCHARIDE HYDROLYSATE BY DIAULTRAFILTRATION. A PILOT PLAN SCALE

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Pectin has a long history of use in the food industry and is now extensively studied for pharmaceutical and cosmetic applications. Pectin derived colon-specific drug delivery systems are more effective and reproducible in comparison with other delivery systems, because pectin is only degraded by colonic microflora. The ability of pectin to add viscosity and stabilize emulsions and suspensions is utilized in a number of liquid pharmaceutical preparations.

Typically pectin production is based on the use of large quantities of expensive and inflammable settling alcohol for the purification of the pectin hydrolysated solution. Moreover the concentration of pectin solution under pressure and high temperature, by evaporation and spirit regeneration requires high consumption of electric power. Hence the high cost of refined pectin has limited the extent, to which pectin is used. As well as the disadvantage of the typical process is a safety problems explosive spirit and vacuum installations.

This work aims to design a new technology, which free of these two consumable and ecological non friendly processes that produce inexpensive pectin, which can be used to develop biobased “smart” polymers for industrial applications (sustained release of drug, pesticides and fertilizers, chemically modified nanomaterials which respond intelligently to the stimuli of light wavelength and intensity, moisture and temperature). As a result of collaboration between scientists at Eastern Regional Research Center, ARS, USDA and Tajikistan Chemistry Institute laboratories, new ideas have emerged to advance technology by incorporating their own recently developed methods into traditional technology in order to produce low cost pectin and reduce pollution caused by the waste stream.

The new process includes flash hydrolysis-extraction of pectin from raw materials; cross flow membrane filtration technology with dia-ultrafiltration (DUF) systems that make it possible simultaneously purified and concentrated the pectin hydrolyzed solution. Flexibility of technological scheme in addition permits to process various types of raw materials and derive wide range of semi-products (crude, human consumable pectin materials containing fiber, pectin gel, neutral sugars containing anticancer phenolic compounds). Moreover the ultrafiltration retenant solution became commercial valuable components of beverages and fruit juices having prophylactic remedy.

Both methods: flash extraction and DUF has been patented-Patent TJ 290 and TJ 197 (2010 and 1998, National Informational Patent Center of Tajikistan Republic).

The study demonstrates the advantage of this technique over typical process of pectin hydrolysis-extraction and other patents (DE 3041096 A1, EP 0426431 A1) in designed hereby Pilot Plan. It was shown that use of polyamide membrane has advantages on the polysulfone one. The invention methods allow producing highly quality pectin (characterized by increased molecular weight and galacturonic acid content) and reduce cost of product, when compared to pectin extracted by conventional heating techniques.

ADSORPTION OF WATER VAPOUR ON ACTIVATED ALUMINA: EXPERIMENTS AND MATHEMATICAL MODELING

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Water adsorption with activated alumina desicants is one of the many separation technologies used for natural gas treating and water removal from industrial gas streams. Due to high surface area, thermal stability, crush srength, and liquied water resistance, activated alumina is a cost-effective desicant.

Recently, the technology of high-efficient desicant production based on the products of thermal decomposition of hydrargillite has been developed in the Boreskov Institute of Catalysis [1]. Such alumina oxide desicants have high surface area (~ 400 m^2/g), optimal pore size (~3.5 nm), and high static adsorption capacity (~24.2% at 25°C). Also, they can be easily regenerated to its original efficiency by heating at temperature 250°C.

In this work the application of alumina oxide dessicants in the process of water vapour adsorption from an air stream in packed-bed adsorber has been studied both experimentally and numerically.

Adsorption eqilibrium isotherms and kinetic data were obtained by a static gravimetric technique. The experiments were carried out in a thermostated microbalance over a fraction of adsorbent (0.25-0.5 mm) within the inlet air humidity interval of 1-60% vol. at temperature of 20°C. The Virial isotherm [2] was used for the fitting of experimental isotherm data. Effective coefficient of adsorption accounting both the effective diffusion coefficient in the pore system and the gas film resistance as a function of gas velocity has been evaluated. Parameters resulting from kinetic experiments were applied for mathematical modeling of adsorption column packed with activated alumina desicant.

Pilot experiments have been carried out to study the influence of operation conditions and determine the optimal technological regimes in adsorption column packed with activated alumina granules (**Fig. 1**). The influence of various process parameters like gas flow rate, residence time, vapour partial pressure, desorption temperature as well as stability tests on the adsorbent capacity and the value of outlet air dew point temperature have been studied.

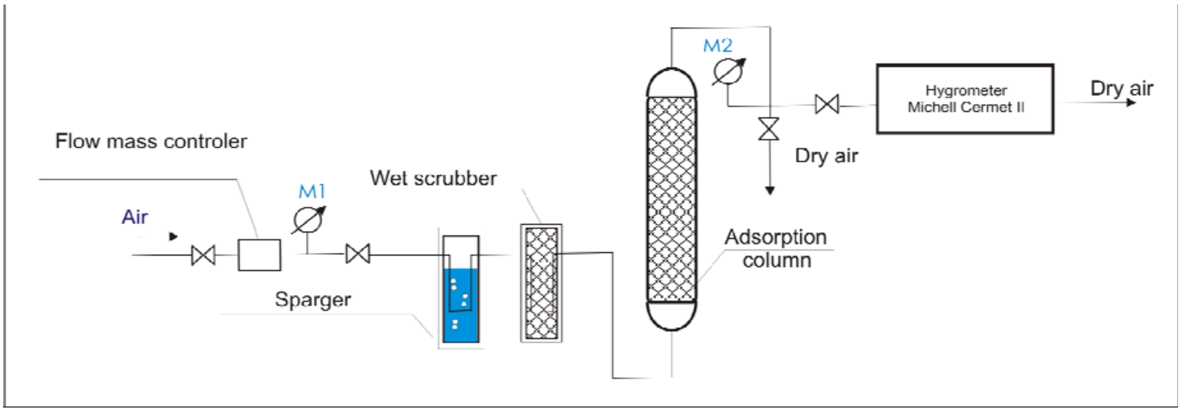

Fig. 1. Sketch of the pilot set-up

The following important observations have been made from the pilot experiments: (1) dew points to -50°C may be achieved with activated alumina at certain operating conditions; (2) the optimal residence time is about 9.0-9.5 s that provides no less than 20 hours adsorption cycle at inlet air humidity 60% to the outlet air dew point temperature - 40°C; (3) initial and final values of adsorption capacity during five cycles of adsorption/desorption practically have not changed.

A one-dimensional pseudo-homogeneous model incorporating with adsorption equilibrium isotherm and kinetic parameters was used for mathematical modeling of adsorption column. The simulated values of outlet air dew point temperature were in a good agreement with ones observed in pilot experiments (**Fig. 2**).

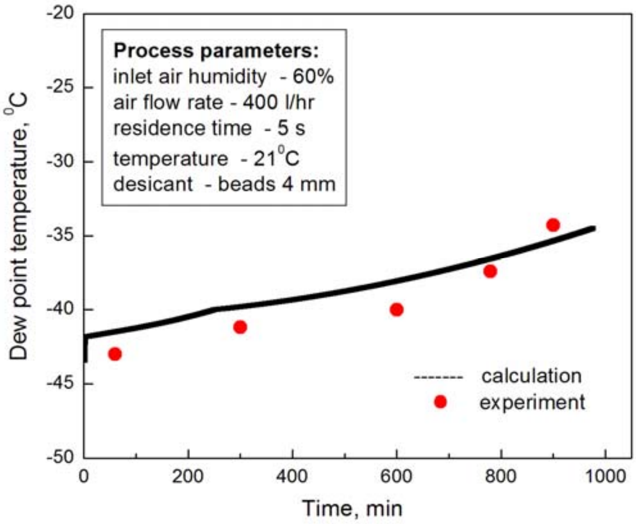

Fig. 2. Comparison of measured and simulated outlet dew point temperatures in adsorption column.

The model has proved the applicability and can be used for optimization of industrial adsorber. As a result, the optimal process parameters in industrial adsorber for water removal from industrial gas streams have been proposed.

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HYDROGENATION OF D-GALACTOSE OVER A Ru/Al_2O_3 USING A SEMI-BATCH REACTOR SYSTEM

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Introduction

Utilization of biomass as an alternative for fossil based fuels has been extensive over the last decade and it can be seen as the main renewable and CO_2-neutral energy source for transportation use in future [1]. However, the richness of molecules included in the biomass offers a much wider possibility for exploitation of wood biomass [2]. Therefore, hydrogenation of D-galactose, originating from hemicellulose, to galactitol over a finely dispersed Ru/Al_2O_3 catalyst was investigated with the objective of studying the kinetics of the reaction.

Experimental

An alumina supported ruthenium (2 wt.-%) catalyst was prepared using the impregnation method. Kinetics of the galactose to galactitol hydrogenation was determined in the batch reactor using following experimental conditions: temperature 105, 120 and 135 °C, H_2 pressure 30, 45 and 60 bar. Volume of the sugar solution was 120 ml and the initial sugar concentration was 0.11 which equals to 2 wt.-% sugar solution. The galactose conversions were determined by using 0.4 g of the fresh prepared Ru/Al_2O_3 catalyst (d_{50} = 40 µm) in each run. First order kinetic models were assumed both for galactitol and by-product formation and a non-linear regression was performed to obtain the numerical values for the activation energies as well as for the pre-exponential factors.

Results and discussion

D-galactose to galactitol hydrogenation follows almost first order reaction in hydrogen (Fig. 1). At higher temperatures the reaction order however decreases somewhat being closer to 0.6. However, a first order model inclusing a rate expression for both D-galactose to galactitol hydrogenation and galactitol isomerization was used for the parameter estimation.

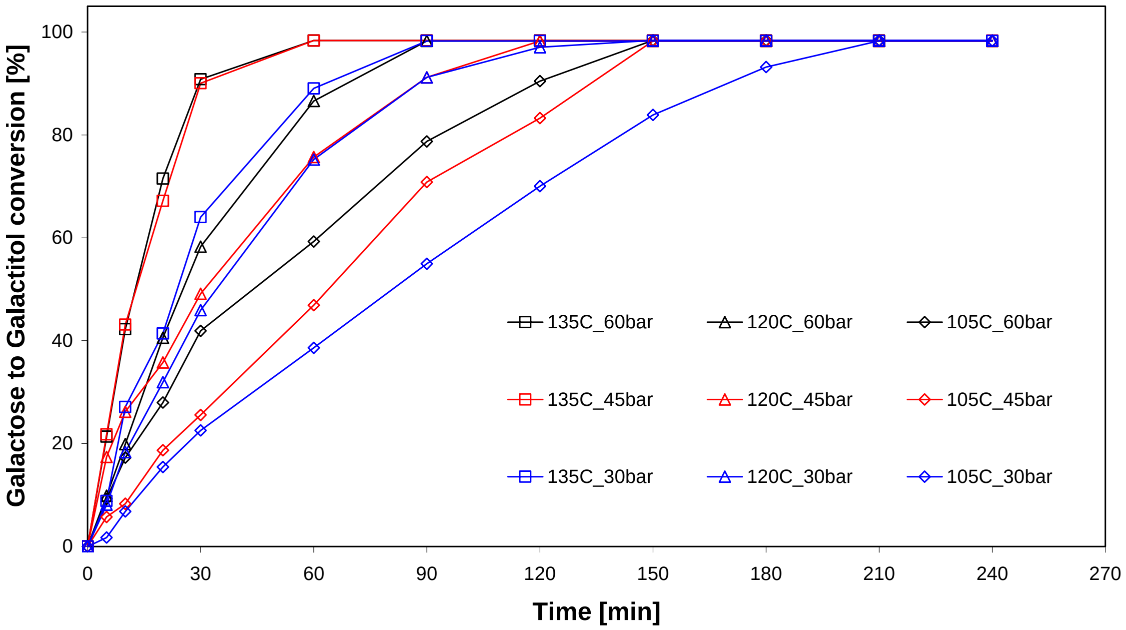

Figure 1. Galactose to galactitol conversion determined in the batch reactor using 105, 120 and 135°C temperature and 30, 45 and 60 bar pressure.

The overall fit of the model shown in was good (R^2 = 0.99) but the estimated relative standard errors for the by-product formation were found to be rather high (Table 1). Overall the model was able to explain the experimental data best at high temperatures and at high hydrogen pressures.

Table 1. Results from the parameter estimation.

R^2 = 99,0	**Estimated Parameters**	**Estimated Std Error**	**Est. Relative Std Error (%)**
A1	2.02E-03	2.63E-05	1.3
Ea1	54200	1390	2.6
A2	1.49E-05	4.12E-06	27.7
Ea2	51000	28300	55.5

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Acknowledgements

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DIRECT ROUTE OF DIMETHYL ETHER SYNTHESIS FROM SYNTHESIS GAS AT MIXED CATALYSTS

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Synthesis of dimethyl ether (DME) from synthesis gas is the actual, in particular to use DME as fuel and/or additives to the fuel. At present, production of dimethyl ether from synthesis gas by the direct method in one reactor with simultaneously formation of methanol and its dehydration is not applied. The aim of the present work was to determine the technological parameters of direct route of producing dimethyl ether from CO and H_2, as well as detailing the kinetic and mechanism of the interaction H_2, CO, CO_2, CH_3OH, DME with the surface of the catalysts.

As a catalyst for methanol synthesis it was used $CuO/ZnO/Al_2O_3$ sample and as catalyst for hydration of methanol was used γ-Al_2O_3 or zeolites. It was established, that a layerwise boot with an intermediate middle layer of catalysts for methanol synthesis and dehydration (1st layer - the catalyst for methanol synthesis, 2nd layer - a mixture of methanol synthesis catalyst and a catalyst for the dehydration, the third layer - the catalyst for dehydration) can significant increase the yield of dimethyl ether during catalysis. It was obtained the optimal parameters of the catalytic process under high pressure: bulk volume of catalyst 5 cm^3, temperature range from 200 to 260 °C, working pressure of 30 Atm, the rate of feed stream of $CO+H_2$ = 48 ml/min, the molar ratio of source gases $CO:H_2$ = 1:2. It is shown that the use as a catalyst (HZSM-5) for dehydration of methanol with a module 30 observed a maximum yield of about 35 – 40 % at T = 220 °C, P = 30 atm (3 MPa), H_2/CO = 2.

Presence of Lewis and Brensted acid sites on the catalyst surface and they influence on the catalytic properties were established. Dehydration of methanol on the surface of the zeolite proceeds with the formation of DME at 234°C, which is the optimum temperature of obtaining DME from CO and H_2 on the industrial catalysts with layered load. It is concluded about the mechanism of the synthesis of DME.

Acknowledgements

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OPTIMIZATION OF OPERATION REGIMES OF REACTOR FOR C_9-C_{14} ALKANES DEHYDROGENATION

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One of the modern sources for producing synthetic detergents for both domestic and industrial uses are the linear alkylbenzenes (LAB). The production of LAB is divided into several stages with separate apparatus operating under different conditions. The modern production process consists of four main stages. On the first stage, alkanes with 9 to 14 carbon atoms are separated from kerosene cut using the molecular sieves (Parex process by UOP Inc.). Clean alkanes then undergo dehydrogenation on Pt/carrier catalysts, producing the alkenes C_9–C_{14}. Dienes, by-products of dehydrogenation, are then hydrogenated to alkenes on Ni/Al_2O_3 catalyst. The final stage is alkylation of benzene with alkenes.

The dehydrogenation stage is the limiting one. Efficiency of this stage defines the overall efficiency of LAB production plant. Modern dehydrogenation catalysts are PtSn/carrier systems, where the carrier is either γ–Al_2O_3 or aluminosilicate [1]. The process requires high temperatures (740–770 K) and slightly raised pressure of approx. 0.2 MPa.

As most oil refinery plants are staffed with automatic control systems and dynamic databases nowadays, the efficient way for optimizing the dehydrogenation process is using the mathematical modeling approach [2]. The mathematical model and its software implementation is developed in Tomsk Polytechnic University to monitor and forecast the LAB production [3]. The model takes process unstationarity into account, as it considers side reactions of coke formation, cracking, izomerization and arene formation, further to dehydrogenation, which makes it more advanced than concurrent models.

Thermodynamic analysis of coke formation reactions proved that these reactions are reversible under dehydrogenation conditions. This means that carbon structures on the active catalytic surface are progressively formed and hydrogenated with active hydrogen that is present in the reactor. Optimal catalytic reactivity under process conditions is achieved, when all the coke structures formed are being destroyed by hydrogenation.

Different alkanes in C_9–C_{14} mixtures are characterised with different reactivities [4]. The contents of dehydrogenation raw stock are constantly changing, portions of different alkanes increase and decrease frequently. Thus, operational conditions can be picked so the least coke amount is formed. In other words, each raw stock composition allows different options of operation for obtaining the same required product yield. The algorithm for calculating the optimal parameters of dehydrogenation using the computer modeling system [5] for dehydrogenation process is presented below.

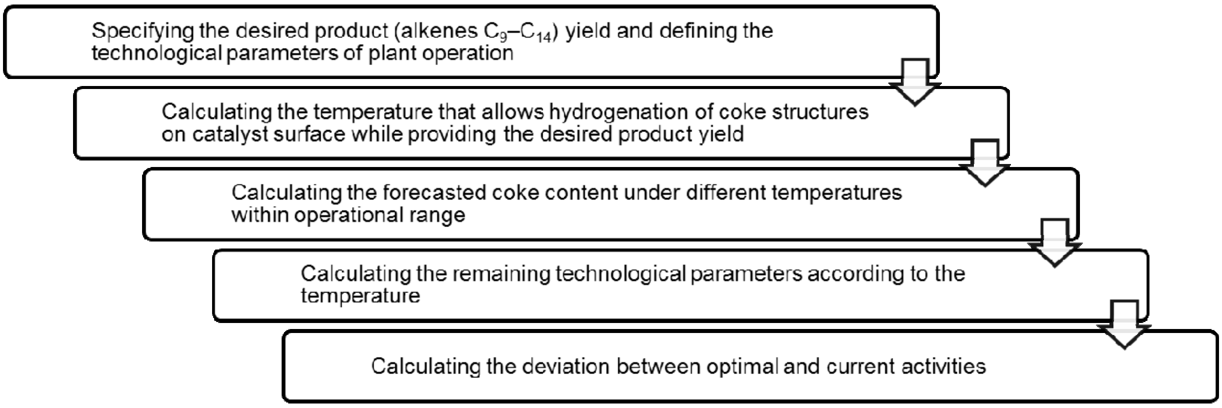

Fig. 1. Algorithm for finding the optimal parameters of catalyst operation.

The calculations have shown that tha catalyst life could be extended by 20–30 % if it is operated closely to optimal activity compared to normal catalyst operation.

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MATHEMATICAL MODELLING OF SOOT DEPOSITION WITH TAKING INTO ACCOUNT PARTICLES SIZE DISTRIBUTION IN DIESEL PARTICULATE FILTERS

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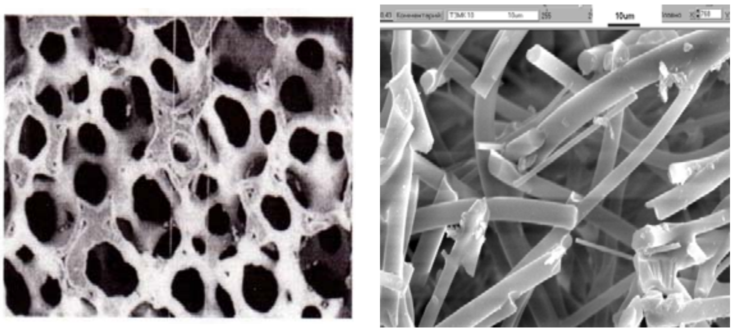
The use of monolith soot filters is very promising to abatement of the amount of soot particles in diesel engine exhaust. Two major groups of filters are use as filter substrates: ceramic wall-flow monolith and ceramic foams.

There are many works, in which mathematical models have been developed for predicting exhaust diesel engine filtration and soot particles deposition. These mathematical models consider three basic mechanisms of soot capture and account for their influence on filtration efficiency: Brownian diffusion, particle interception and inertial impaction. However, mean aerodynamic diameter of soot particles is use in these models. It is well known that different size particles may be presents in exhaust diesel engine: from a few nm up to a few tens μm, depend on engine type, fuel kind and operating conditions. Particle size distributions obtained with a modern Common-Rail Diesel (Peugeot 406 HDI) at different operating condition is shown [1]. The size of these particles range from 20 to 250 nm or even larger, the mean aerodynamic diameter is nearly 0,1 μm. Brownian diffusion is efficient in capturing small particles and interception and inertial impaction are efficient for large particles. So we incorporate into the model the size distribution of diesel soot particles.

The mathematical model includes unsteady-state differential equations for polydisperse soot particles, O_2 and CO_2 concentrations in gas phase, soot content in solid phase, filter temperature and pressure drop. The heat balance accounts for heat transfer through convection and heat release by soot oxidation. Mass balances of gas phase compounds (soot, O_2, CO_2) include mass transfer through convection, changes in O_2 and CO_2 concentrations due to soot oxidation, decrease in soot concentration because of collecting of polydisperse soot particles by means of inertial impaction, interception and Brownian diffusion. Deposited soot equation takes these mechanisms into account as well.

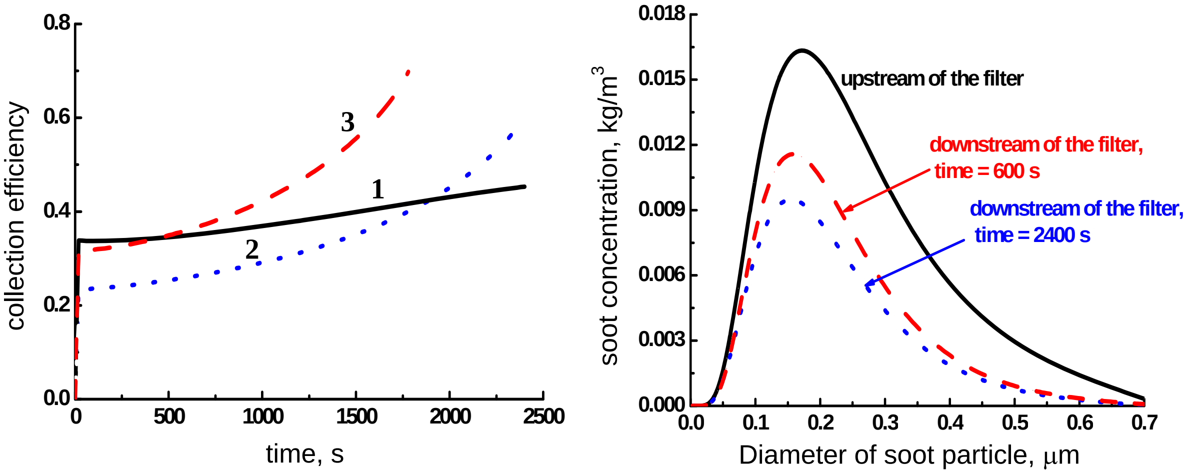
We considered two filter substrates (foam and fibers (fig. 1)) and two particle size distributions corresponding to both diesel exhaust gases of modern passenger cars and gases generated by acetylene-burner.



a) *b*)

Fig. 1. Micrography of the filtering substrates
a) mullite [1]; *b)* fiber quartz

Figure 2 illustrates the results of the mathematical modelling of soot collecting in fiber quartz wall-flow monolith with the next operating condition: exhaust flow rate = 0,1 m/s, exhaust temperature = 200 °C, soot feed concentration = 0,13 g/m^3, median particle diameter = 0,17 μm, standard deviation of particle size distribution = 1,74, O_2 concentration = 8 % vol., wall thickness = 0,43 mm. It may be useful to plot the collection efficiency as a function of the time (fig. 2a). The solid curve shows the collection efficiency obtained with the taking into account polydispersity of soot particles. Dash and dot curves were obtained with mean aerodynamic diameter of the particles. One can see the significant deviation of solid curve from the others. Figure 2b shows the particle size distribution of the exhaust aerosol upstream of the filter and downstream of the filter. The mean particles diameter was decreased after 2400 s from the beginning of the filtration process.



a) *b*)

Fig. 2. The influence of polydispersity of soot particles on the collection efficiency:
a) the dependence of the collection efficiency on time: 1 – with taking into account polydispersity of the particles; 2,3 with mean aerodynamic diameter, 2 –0,3 μm, 3 – 0,4 μm;
b) particle size distribution

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POSTER PRESENTATIONS

SECTION III

Chemical Reactors and Technologies for Emerging Applications

CATALYTIC COMBUSTION OF MUNICIPAL SEWAGE SLUDGE IN CATALYTIC FLUIDIZED BED REACTOR

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Wastewater sludge is a slurred organic-mineral substance of high water content (99.5-99.7%) and it contains a wide variety of chemical elements, including heavy metals [1]. A lot of organic and inorganic components in sludge possess mutagenic activity; pathogen or disease-causing microorganisms can threat human health. For this reason, agricultural use of the sludge is limited or completely forbidden all over the world [2 - 4].

Incineration is a generally applied thermal treatment technique, whereas pyrolysis and gasification are still under development [4]. The technology of deep oxidation of solid fuels and wastes developed at the Institute of Catalysis is free of major disadvantages of high-temperature combustion and enables to conduct the process in autothermal regime (i.e. without additional fuel) at water content in sludge about 75% wt., to reduce specific quantity of metal of equipment more than 15 times, to eliminate or sharply reduce formation of gas emissions of toxic organic compounds, oxides of carbon, nitrogen and sulfur.

Experimental investigations of sewage sludge catalytic combustion were carried out using laboratory unit. A number of experiments were carried out using catalysts (IK-12-70 ($CuCr_2O_4/\gamma$-Al_2O_3) or IK-12-73 ($CuMgCr_2O_4/\gamma$-Al_2O_3) with size of the spherical particles 1.5-2.0 mm) or quartz sand with average diameter of the particles 1 mm. In experiments sewage sludges of Novosibirsk, Omsk and Moscow were investigated. Experimental samples of sewage sludges were previously dried at 120 °C and after that were ground. The fraction less than 1 mm in diameter was used in the experiments. The outlet gases and combustion products were analyzed using modern analytical device and standard testing methods.

Results and discussion. The elemental analysis showed that dry sludge to 39-40% wt. consists of mineral components and 60-61% wt. of organic (sulfur, chlorine and phosphorus). There are more than 20 different elements in mineral part of sludge. The primary elements of mineral residue are Fe, Si and Zn (about 10-50 %). Content of Al, Ca, K in residue is about 1.0-10%. Amount of Zr, Y, Sr, Rb, Cu, Ni, Cr, Mn, Ti, S in residue is 0.1 – 1 % and Pb, Hg, Cl, P is less than 0.1 %. Burn-out degree and outlet gas concentrations depended on reaction temperature at constant contact time in reactor equal to 0.95 s. Comparison of these results are shown in Table 1.

Table 1. Characteristics of outlet gases and ash received during catalytic and non-catalytic combustion in fluidized bed reactor with diameter 40 mm

Temperature, °C	**Catalytic combustion**			**Combustion in bed of sand**		
	500	600	700	500	600	700
Specific remain's surface, m^2/g	24	57	97	19	23	7
Burn-out degree, %	94.0	98.2	99.5	68.2	89.4	98.5
Concentration of NO_X, mg/m^3	-	18.8	22.7	17.0	198	277
Concentration of SO_X, mg/m^3	-	-	-	-	30	163

In addition, presence in sewage sludges of toxic chlorine compounds during non-catalytic combustion in bed of inert sand can result to formation of significant concentrations of chlorinated benzodioxins and benzfurans. In contrast to it the contents of the most dangerous 2,3,7,8 – tetrachlordibenzdioxin and 2,3,7,8 – tetrachlordibenzfuran in outlet gases at catalytic combustion were found below of detection limit of analytical device (less than $10\ 10^{-9}$ mg/m^3). This concentration values is significantly lower than the same according to accepted in USA regulations of dioxines content in atmosphere ($100\ 10^{-9}$ mg/m^3).

It can be concluded that catalytic combustion results to the most effective burn-out of residue, sharply reduces outlet concentrations of CO, NO_x, SO_x due to its fixation with mineral residue. Concentrations of dioxins don't exceed international regulations. Thus the technology of catalytic combustion of sewage sludges in fluidized bed of catalyst can be successfully applied for environmentally safe treatment of hazardous sewage sludges.

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PP-III-2

TECHNICAL CHARACTERISTICS OF THE HYDROGEN–FILTERING MODULE ON A BASE OF THE PALLADIUM FOIL

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Technical characteristics on productivity and selectivity developed by authors hydrogen-filtering module on the basis of thin Pd foil were investigated. This module is intended for use in structure of membrane reactors, and also for producing of highly pure hydrogen as a fuel for different objects of hydrogen power engineering and transport. The design of hydrogen-filtering membrane module is executed as a package with filtering disk from a Pd/Ag (15 wt %)-foil of 30 μm thickness placed between two stainless steel grids, which have 130 μm thickness and average pore radius of 2.0 μm, that provided its high mechanical strength. Filtering characteristics were studied at the temperature range of 25-550 °C and pressure drop up to 176.5 kPa.

It is established that the effective magnitude of an activated energy is about 10.9 kJ/mol i.e. it is similar to *E*a values given the literature for palladium composite membranes. The study of H_2 filtration from binary mixtures of H_2 with other gases (Ar, C_3H_8, N_2) has shown that these gases don't influence on the permeability. Low activation energy of process testifies that hydrogen transport through of the membrane is not accompanied by formation of strong chemical bonds with a membrane matrix, i.e. defining dynamics of the filtration process is, apparently, physical (Van-der-Vaals) adsorptions-desorption of hydrogen. It is shown that filtering ability of the membrane module is close to the literature values for Pd composition membranes, but the foil membrane have more high stability, mechanical durability and manufacturability of product fabrication. Authors plan to move from the stage of manufacturing of experimental samples to a stage of experimental-industrial fabrication of hydrogen-filtering of modules with membrane elements of 30, 20, and 10 μm thickness.

OPTIMIZATION OF FIBER-GLASS CATALYTIC MATERIALS FOR PURIFICATION OF STYRENE FRACTION FROM IMPURITY OF PHENYLACETYLENE BY THE SELECTIVE HYDROGENATION METHOD

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We investigated influence of the glass fiber woven carrier chemical composition and method of its preliminary activation for the key parameters of the catalytic purification of styrene fraction from phenylacetylene impurities. It was found a significant increase in activity and selectivity of the catalytic material as a result of doping of the woven matrix by defined set of metal oxides and using of operations of dosed pre-processing of carrier in etching media.

PP-III-4

PARTIAL OXIDATION OF NATURAL GAS IN AXIAL AND RADIAL REACTORS

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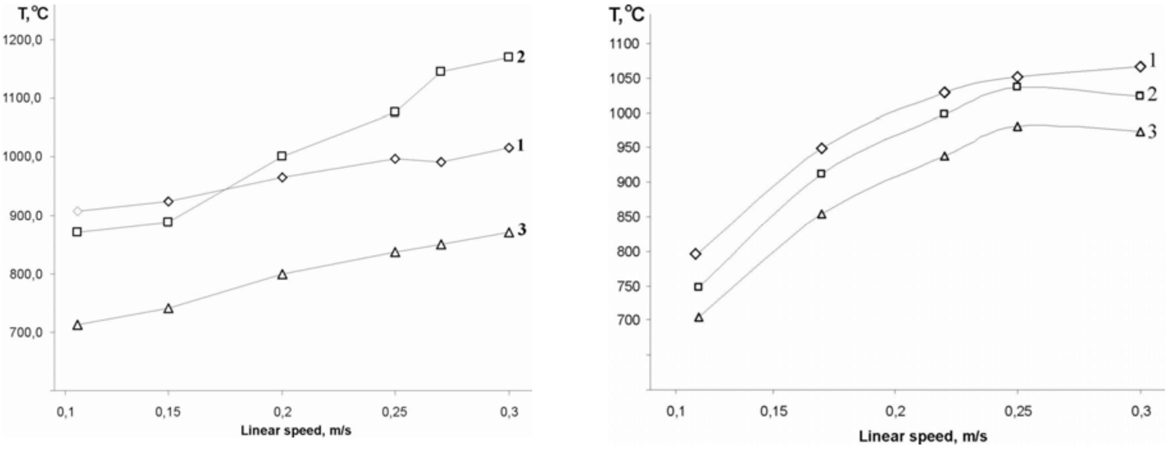
Partial catalytic oxidation of natural and petroleum gases over block catalysts at small contact time is a promissing process for the syngas production in compact reactors. Partial oxidation of natural gas (92 %vol. of methane and C_{2+}-hydrocarbons up to balance) into syngas was studied in two types of reactors, i.e. axial and radial ones. Oxidation of natural gas was carried out in autothermal conditions. Porous blocks prepared by the self-propagating synthesis were used as monolith catalysts. Chemical composition of metal-ceramics was Ni – 52,9 %wt, Al_2O_3 – 5,0 %wt, MgO – 17,2 %wt, $MgAl_2O_4$ – 14,9 %wt, ZrO_2 – 9,5 %wt, CaO – 0,5 %wt, the catalyst porosity was 55-60 %. A disk-like shape of the catalyst block was used for axial reactor, while quill cylinder was used for radial reactor with entering of reaction mixture inside of cylinder. The reactor was equipped with gas-distributing device for balancing of gas flows. The volume ratio of natural gas/air was varied in range of 1,0/2.4–2.9, linear velocity of reaction mixture pass through the catalyst bed was varied from 0.1 up to 0.3 meter per second.

The natural gas conversion was 75-82 % at 70 % selectivity towards H_2 and CO for axial reactor at cool reaction mixture (T= 80 °C). To reach the methane conversion higher 90 %, the gas mixture should be preheated up to temperature of 250-350 °C. In the radial reactor at similar initial parameter ($T_{\text{input gas}}$ = 80 °C) the natural gas conversion was more then 90 % due to the internal heat recuperation. The initial reaction mixture during experiments in radial reactor was not preheated.

In the axial reactor the increase in reaction mixture speed above 0.15 m/s led to the shift of maximal temperature from reactor input to the center of the catalyst bed. While the linear velocity of reagent flow was increased, the temperature gradient in the catalyst bed was enhanced and reached 300 °C (Fig. 1). Methane conversion increased with increase in the linear velocity of reagent flow, and deareased at 0.2 m/s (Fig. 1). Pressure drop along the catalyst bed increased 6.1 times for 0.3 m/s in comparison with 0.12 m/s linear speed of the reagent flow.

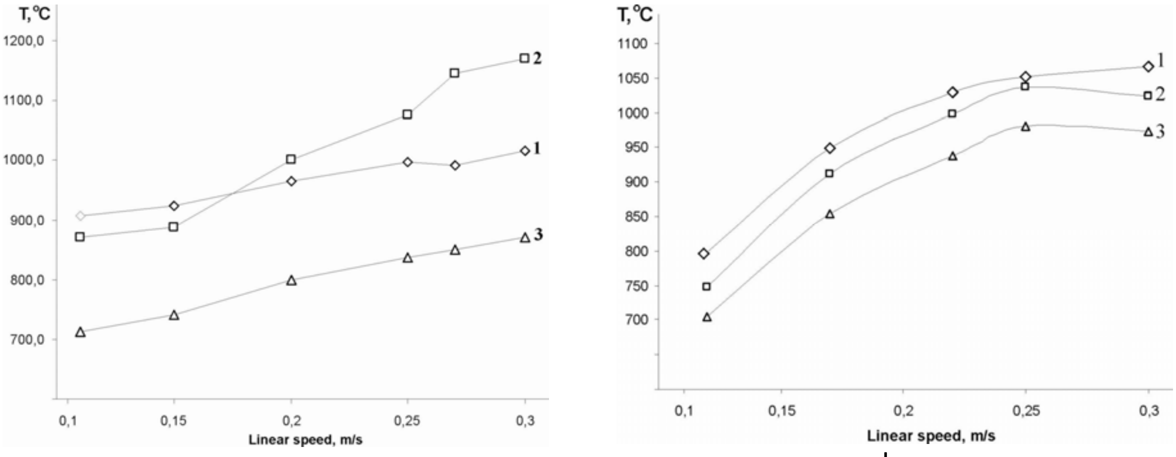
Selectivity towards hydrogen and CO did not depend on the linear velocity of reagent flow in conditions of the radial reactor. Methane conversion increased steplike at the linear velocity increase. Subsequent enhancement of the linear velocity led to minor conversion changes (Fig. 2).



a. b.

Fig. 1 Dependence of the temperature of the catalyst block (1 – input of the catalyst block; 2 – the center of catalyst block, 3 – output of the catalyst block) on the linear velocity of the reagent flow: (a) axial reactor, (b) radial reactor

While the liner speed of the reagent flow increased, the temperature of the catalyst bed raised. The temperature gradient along the catalyst bed was practically constant in all range of linear speed varying and was less than 100 °C (Fig. 2). Pressure drop along the catalyst bed was 261 Pa at 0.12 m/s and 980 Pa at 0.3 m/s.



a. b.

Fig.2 Dependence of natural gas conversion (1), selectivity towards CO (2), selectivity towards H_2 (3) on the linear velocity of reagent flow: (a) axial reactor, (b) radial reactor

Acknowledgements

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ANISOLE HYDRODEOXYGENATION OVER Ni-Cu BIMETALLIC CATALYSTS: EFFECT OF Ni/Cu RATIO ON SELECTIVITY

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Fast pyrolysis, which allows to produce liquid organic products with the high yield, is considered to be the promising approach for processing of lignocellulosic biomass. However, pyrolysis oil (or bio-oil) can not be used as a fuel or fuel additive due to the high oxygen content (20 – 40%) results in such undesirable properties as low thermal and chemical stability, low heating value, immiscibility with the fossil fuels and high acidity and requires to be upgraded by oxygen removal and increasing of hydrogen content. There are two general routes for pyrolysis oil upgrading -hydrodeoxygenation and catalytic cracking. It was shown previously [1] that the Ni-Cu catalysts are active in hydrodeoxygenation of bio-oil and its model compounds. Thus, the purpose of the present study was to investigate the effect of Ni content the active component of Ni-Cu bimetallic catalysts on the selectivity of anisole conversion products formation; anisole represents the model compound for lignin depolymerization products in pyrolysis oil. In order to obtain the alloys with the homogeneous phase composition the catalysts were prepared by simultaneous decomposition of metals salts with subsequent stabilization with 10% wt. SiO_2. The reaction was carried out in the excess of hydrogen in batch reactor at 280°C and 6 MPa. On the basis of obtained kinetic data the reaction scheme of anisole conversion was proposed, which includes two parallel routes, one of which leads to C_{ar}-O bond cleavage with the formation of benzene (HDO route), the second - hydrogenation of the aromatic ring of anisole with the formation of methoxycyclohexane and cyclohexanol (HYD route). According to the proposed reaction scheme the dependence of the first-order rate constants for the two routes on the nickel content in the active component of the catalysts was determined (Fig.1).

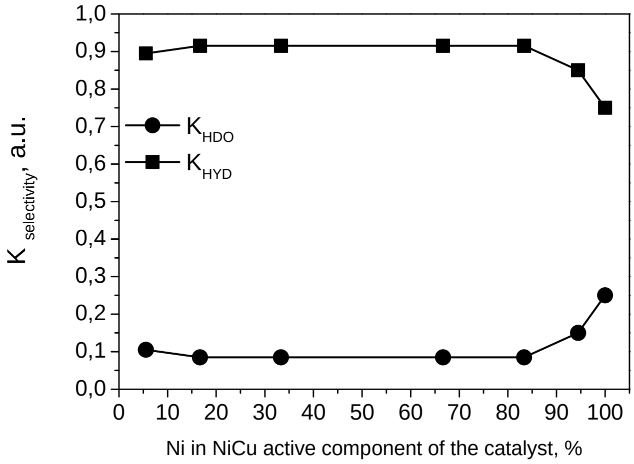

Fig. 1. The selectivity towards the HDO and HYD products formation vs. the nickel content in the Ni-Cu catalyst.

It is shown that for the samples with the high nickel content Ni / Cu ratio increase leads to the increase in the rate of HDO products formation and decreases the rate of HYD products formation. At the same time the specific activity in anisole conversion became lower at the higher Ni / Cu ratios, which may be due to the deactivation of catalysts as the result of the carbon deposits formation on the surface.

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Acknowledgements

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PP-III-6

THE PERFORMANCE OF AN AERATED STIRRED TANK REACTOR ON VHG BATCH FERMENTATIONS

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The quest for new and renewable energy sources has greatly increased due to the depletion of fossil fuels reserves. Agro-food wastes appear as a cheap and renewable energy source that can contain great amounts of carbon to be transformed in bioethanol that can be used as additive to gasoline. Industrial wastes of carob pod have a large content in carbohydrates that can be ferment into ethanol. *Saccharomyces cerevisiae* yeasts have been widely used in fermentation processes for bioethanol production because of its considerable tolerance to high concentrations of ethanol and sugar content and low pH values [1]. The scope of this study was to evaluate the performance of an aerated stirred tank reactor, when fermenting carob pod extract at high sugar concentration. Batch fermentations were carried out in a reactor with 2.4 l of carob syrup with 250 g/l in sugar content and supplemented with peptone and yeast extract at low concentrations, at two different aeration rates in order to verify the positive influence of different aeration flux, the tank geometry and mixing efficiency for high ethanol yields. Results showed that at a higher aeration rate, such as 0.63 vvm, ethanol production reaches its maximum of 70.7 g/l with a yield of 0.3 g of ethanol per g of substrate and *S. cerevisae* growth figured a specific growth rate of 0.1 h^{-1}. This production fell short of the expected and theoretical yield of 0.51 g ethanol/g substrate, while at 0.13 vvm of aeration rate ethanol production reached 110.6 g/l showing a yield of 0.45 g ethanol/g substrate.

Carob extract fed-batch fermentation was carried out, at 30 °C, 250 rpm and 0.13 vvm of aeration rate, to improve ethanol production by addition of fresh medium and alleviate ethanol toxicity due to the dilution of the medium. At the first stage of this fermentation ethanol content reached 67.0 g/l with a yield of 0.48 g ethanol/g substrate and a cellular growth with a specific growth rate of 0.226 h^{-1} was noticed. After 20 hours of fermentation 0.75 l of carob extract medium was added providing more carbon source for ethanol production. Cells continued to grow at 0.079 h^{-1} and ethanol concentration reached 99.6 g/l after 50 hours of fermentation with a yield of 0.47 g ethanol/g substrate. After a second addition at 50 h, ethanol concentration increased and reached its maximum of 126.7 g/l at 120 hours with a yield of 0.50 g ethanol/g substrate. In this third stage, cellular growth was observed with a specific growth rate of 0.011 h^{-1}. During these three stages total sugar consumption increased progressively from 47.6 % to 52.0 %, reaching 61.8 % at the last stage, while at the batch fermentation 89.0 % of the available sugar was consumed. Ethanol productivity at the batch fermentation was 2.04 $g.l^{-1}.h^{-1}$ however, at fed-batch fermentation ethanol productivity reached 3.64 $g.l^{-1}.h^{-1}$ at the first stage, decreasing harshly within the next two stages achieving values of 0.65 $g.l^{-1}.h^{-1}$ and 0.69 $g.l^{-1}.h^{-1}$. These results show that carob pod was successfully used to produce bioethanol, using a STR and mild aeration. Major production occurs during exponential growth phase, but higher values of ethanol content it's possible at stationary phase. Although fed-bath fermentation has lower ethanol productivity, fresh medium addition showed to be an excellent way of enhancing ethanol production from 110.6 g/l to 126.7 g/l due to the decrease of ethanol toxicity and higher availability of total sugar.

High aeration flux promotes entrainment of ethanol in the gas stream of exhaust gases from the reactor. One way around this constraint is through the use of lower aeration flows, and the inclusion of an efficient condenser, with high capacity, in the exhaust gas output, minimizing losses evaporation. This design improvement, coupled with fed-batch operational mode, may improve substantially the fermentative performance of the ethanol production on VHG systems.

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PP-III-7

CONVERSION OF WAXES FORMED DURING THE FISCHER TROPSCH PROCESS TO DIESEL FUEL

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Fischer-Tropsch process can be considered as a interesting opportunity for liquid fuel production, unfortunately a large amount of heavy hydrocarbons is formed in this process.

However, heavy waxes can by transformed to the liquid hydrocarbon by cracking-isomerization process. Due to increasing prices of natural oil many research efforts are focused on this process. Paraffin cracking usually is conducted over elevated pressure and in the temperature range 300-500°C over bifunctional catalysts which have ability to cracking, isomerization and hydrogenation. Hydrogenation process requires metallic centers on catalysts surface. However isomerization and cracking process needs the acidic centers on catalysts surface.

The main goal of this work was to determine the effect of wax type on the liquid product composition, as well as yield of hydrokraking process.

Catalytic hydroconversion of parafine were carried out using different source: hexatriacontane (99,9% $C_{36}H_{74}$) LTP56-H, Sasolwax M5. Conversion process were carried out over mordenite supported platinum (1-5%Pt) catalysts, under pressure (initial 60bar) in the temperature range 300 - 360°C in stirred high pressure reactor. Process time was in the range 0,5 - 4 h. Products composition were determined by GC-MS chromatography.

During hydroconversion of paraffin three processes took place simultaneously: hydrocracking, hydroisomerization, and aromatization. Due to this reason in process product the presence of alkanes, isoalkanes and aromates was confirmed. Reaction time plays a crucial roule on the product distribution. Increasing of process time lead to the formation of large amount (up to 70%) of aromatic compound. Process temperature also changes the product composition significantly. It was confirmed that increasing the reaction temperature from 300 to 360°C leads to the formation of light hydrocarbon (containing no more than 9 carbon atom in molecule) with the large contribution of aromatic compound.

Catalysts acidicity strongly affects on paraffin conversion and hydrocarbon distribution in the final product. Increase of surface acidicity caused the increase of conversion degree of the paraffin.

Comparison of liquid product obtained from the conversion process of different paraffin leads to the conclusion that there is no significant differences in product dependently from paraffin composition.

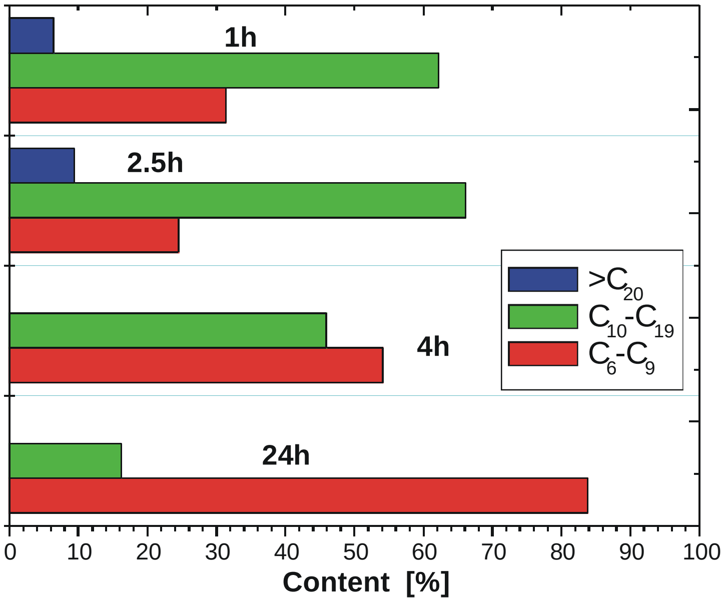

Fig. 1. The influence of reaction time on the product composition over 1%Pt/Mordenite catalysts in $C_{36}H_{74}$ hydroconversion (T=340°C, p=60 bar)

The activity tests carried out for catalytic systems showed that process yield depends strongly from the platinum loading. However increase platinum content above 2%$_{wt}$ causes a significant increase of light hydrocarbon content in the final product.

Partial financial support from grant number NR 05-00-88-10/2010 is gratefully acknowledgement.

HYDROCRACKING OF WAXES TO FUEL FRACTION OVER BIFUNCTIONAL ZEOLITES CATALYSTS

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Shrinking resources of natural gas and crude oil in recent years led to increased interest in alternative fuel generation technologies. One possible solution is conversion of waxes products obtained during Fischer-Tropsch synthesis to the components of motor fuels over bifunctional catalysts containing zeolite and metallic component.

The aim of this work was to determine the catalysts composition (type of zeolite and active phase) and reaction parameters on catalytic activity in hydrocrackig process and physicochemical properties of prepared systems.

In order to achieve the intended purpose the monometallic nickel and platinum catalysts supported on various zeoliotes (NH_3-mordenite and BETA-zeolite) were prepared by conventional impregnation methods. The nickel content was 0.5, 1.5, 5, 10% wt., platinum content was 1% wt. The physicochemical properties of catalysts were examined by BET, XRD, TPR and TPD-NH_3 methods. Chemisorption uptakes were measured using ASAP 2020C apparatus from Micromeritics (USA). Catalytic activity were performed in stirred high pressure reactor. The inintial pressure of the process was 6Mpa, hydrocracking process was run by 1, 2.5, 4 or 24h. The product composition were determined by GC-MS technique.

Results and discussion

The activity tests carried out over bifunctional platinum and nickel supported catalysts in hydrocracking process showed that platinum catalysts require lower temperature to achieve higher content of fuel fraction in liquid product in comparison to nickel catalysts. The increase of the reaction temperature leads in all cases to create products with small amounts of carbon atoms forming a hydrocarbon and increase of cyclic and aromatic hydrocarbons in the final product, with a decrease in the content of branched-chain hydrocarbons.

It was found that extending the process time leads to a significant increase in the share of hydrocarbons of low number of carbon atoms and at the same time caused the increasing of the aromatic compounds content in the product. Conducting of the hydrocracking process for 24 h caused formation a product containing hydrocarbons with less than 10 carbon atoms in the molecule, while they are mainly aromatic compounds.

Increasing the reaction pressure from 6 to 9 MPa has no significantly influence on the distribution of hydrocarbons in the liquid product. The increasing of the reaction pressure affects significantly on the nature of formed product and leads to an increased iso alkanes in the final product, while reducing the aromatic content.

Nickel and platinum introduction does not change significantly the specific surface area of zeolites. The reduction studies of nickel and platinum supported catalysts showed only reduction profile coming from nickel oxide reduction. It was observed that nickel exist on the surface in various form which differ interacted with the support. The XRD studies confirm the presence of crystalline form of mordenite, as well as in the case of highly loaded nickel samples the presence of NiO phase (for catalysts containing 5 and 10% of Ni). The result of basicity measurements show one wide desorption effects in temperature range 150 - 450 °C. Introduction of nickel decreases the amount of sorbed ammonia. In the case of catalyst containing 10%wt of Ni about 50% decrease of desorption peak area in comparison to zeolite was observed.

The results of TPD-NH_3 measurments carried out for nickel and platinum catalysts used in hydrocracking process indicate the important role of the type of support on the process. The high total acidity of catalysts promotes the processes of cracking and isomerization of waxes, leading to the formation of direct products of aromatic and branched hydrocarbons containing small number of carbon atoms in the molecule (compounds containing in the molecule from C_6 to C_{10}).

Acknowledgements

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PP-III-9

HYDROGEN PRODUCTION FOR FUEL CELLS TECHNOLOGY BY STEAM REFORMING OF METHANOL

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Introduction

The increase in demand for energy derived from the processing of natural fuels (coal, oil and gas), and thus increasing emissions of CO_2 and other greenhouse gases leading to global warming, caused in recent years the development of research into finding alternative energy sources. One possibility to replace natural fuels is hydrogen, whose combustion does not result in CO_2 emissions.

Hydrogen can be used to power fuel cells installed in vehicles, turbines, generators or heating equipment. It can be also used as fuel in hybrid, turbine or internal combustion engines. It is a valuable substrate for many other chemical processes such as ammonia synthesis, methanol synthesis, and synthesis of higher hydrocarbons, aldehydes, ketones, carboxylic acids or esters [1, 2].

Experimental

The monometallic palladium, nickel, ruthenium and copper catalysts supported on $ZnAl_2O_4$ were prepared by conventional impregnation methods. The binary oxide $ZnAl_2O_4$ was prepared by co-precipitated method. The obtained support material was impregnated by appropriate aqueous solution of metal salts. Then the catalysts were dried and calcined 4h in air at 400 °C. The physicochemical properties of prepared catalysts were examined by BET, XRD, XPS and TPR methods. Chemisorption uptakes were measured using ASAP 2020C apparatus from Micromeritics (USA). The activity tests in methanol steam reforming (SRM) and methanol decomposition were carried out over all catalysts in the temperature range 160 to 320°C in a flow quartz reactor under atmospheric pressure, molar ratio $H_2O/CH_3OH = 1$.

The aim of this work was to determine the influence of catalysts composition on catalytic activity in decomposition and steam reforming of methanol reactions.

Determination the relationship between physicochemical properties and catalytic activity in both remaining above reactions was alsothe purpose of this work.

Results and discussion

We prepared monometallic Cu, Ni, Ru, Pd/ $ZnAl_2O_4$ supported catalysts using impregnation method and we tested these systems in methanol steam reforming reaction and decomposition of methanol. Activity tests carried out for monometallic Cu, Ni, Ru, Pd supported on binary binary oxide catalysts showed that all catalysts were active in methanol steam reforming reaction (SRM) and the highest conversion of methanol exhibited Cu, Pd and Ni catalysts. We studied also the influence of copper concentration on catalytic activity in SRM reaction using (2, 5, 20)%Cu/ $ZnAl_2O_4$ catalysts and we observed that conversion of methanol depends strongly on the metallic surface area of copper. The highest yield exhibited 20%Cu/$ZnAl_2O_4$ system, which had about 50% methanol conversion at 200 °C. We observed that catalysts with the highest metallic surface showed the higher hydrogen yield and conversion of methanol at lower temperature in comparison to other systems. Additionally, the same tendency was observed in the case of nickel and palladium supported catalyst. However, it is worth to note that comparison of copper catalysts and other metal catalytic systems leads to conclusion that only in the case of copper catalysts carbon monoxide was not formed. While, palladium supported catalyst exhibited the best performance in hydrogen formation in comparison to remaining noble metal systems. From the applicability point of view methanol steam reforming is favorable on copper catalyst due to no CO formation and low cost.

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Acknowledgements

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PP-III-10

GRAVITY FLOW DYNAMIC METHOD FOR HYDROLYSIS AND EXTRACTION OF PECTIN FROM SUNFLOWER

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The world consumption of pectin is 18.000-19.000 metric tons and it's important in the food and pharmaceutical industries. All vegetable raw materials with high pectin content are suitable for the production of pectins. For the industrial production the prime sources are apple pomace, citrus peels and sugar beet chips. With increased awareness of obesity, cancer and an aging population, low-calorie foods and low-sugar foods are preferred. This has promoted the use of other sources of pectin like sunflower head residue (SHR) pectins in food industries. The low methoxyl (LM) nature of SHR pectin extends its applications into the business of health foods and functional foods, such as in the manufacture of low sugar jellies, low calorie yogurt and confectionery jelly products. In addition, gels from LM-pectin are thermally reversible.

SHR pectins were usually isolated from raw materials by a static method using sodium hexametaphosphate (SHMP) as the quarantine reagent [1,2].

The objective of this study was to compare the dynamic, kinetically extraction process with the conventional batch process, with emphasis on the SHR pretreatment effect of calcium displacement by sodium, salt forms, concentration and hydrolysis pH on pectin recovery and quality. In the present study, sodium salts: sodium chloride from rock salt and SHMP, was used for pretreatment of raw SHR to further intensification of pectin extraction. There are abundant rock salt reserves available in the Tajikistan. The capability of sodium chloride to intensified pectin extraction from SHR was compared with that of SHMP in order to further lower the cost of pectin production. Furthermore a kinetic (dynamic) method was applied for the extraction of SHR pectin from sun-dried sunflower heads harvested in Tajikistan. The efficacy was compared with that of static method.

Mathematical modeling of ion exchange was used to provide a scientific knowledge base concerning the mass transport mechanisms, which are involved in the calcium exchange from plant cell wall in dynamic and static mode. In an ideal case, the system formulation parameters required to achieve a certain, desired ion exchange profile can be predicted. The kinetically data very well fitted, with R^2 0.999, in the model, showing second order kinetics of the static ion exchange process. The exchange process in static mode govern by second order exchange reaction, although has rate values of the same order of magnitudes as dynamic mode, bud different dimensionalities, which couldn't comparable. In contrary Na^+ ion in labile chorine anion form shows proactive effect for both calcium ion exchange in the first process than for pectin substances (PS) extraction in kinetically favorable mode. Increase of salt concentration at first process hold particular promise for further PS extraction progress and reduce pectin aggregates.

The results of PS and pectin gel (PG) fraction obtained in the pH 2.0 demonstrated that Mw and [η] of the soluble fractions randomly changes from one fraction to another. From all fraction the fraction 1, 3, 4 and 5 has high value of Mw ranging from 124.3 KD to 161.5 KD and [η]. However the gel fraction has low Mw with narrow distribution.

Thus we are making a conclusion on superior of a newly developed method for pectin extraction from sunflower head residue, using low cost salt NaCl instead traditionally SHMP, which provide favorable condition for high pectin yield with good quality in mild acidic condition. Also application of dynamic method of extraction will make the new method more attractive for the commercialization of results.

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PP-III-11

METHOD OF CLEANING OF CRACK SURFACES OF NICKEL-BASED ALLOY PRODUCTS

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The operation of aviation gas turbine engines is accompanied by formation of cracks on the turbine blades caused by high temperatures, high aerodynamic and mechanical loads, etc. The blades are very expensive. Therefore, the development of repair-recovery technologies aimed at extending the blade service life is one of the topical problems in the turbine construction.

At present, the DAYTON method is widely used to recover cracked metallic parts, which permits one to considerably prolong service life of the above parts, to save materials and to reduce labour inputs [1a, b]. The DAYTON recovery is performed via two steps: cleaning of the crack surface from metal oxides; high-temperature soldering of cracks using special heat-resistant solders. Thus, the cleaning of cracks from metal oxides is a necessary condition for repair of details with cracks using the high-temperature vacuum soldering method.

The researchers of the Institute of Catalysis and the Institute of Hydrodynamics (SB RAS) performed a series of works aimed at developing a new cleaning method of micro cracks of metallic materials using a nickel-based alloy as an example [2a, b, c].

Fig. 1. Reactor
H = 210 mm, D = 70 mm

Experiments were carried out using the samples of alloy containing 56-64 % wt. of nickel as a basic metal, as well as 8,0-9,5% Cr, 9,5-11,0% W, 9,0-10,5% Co, 5,1-6,0% Al, 2,0-2,9% Ti, and 1,2-2,4% Mo. Simulator samples worked up in the operation conditions of air engines turbine blades were provided by the researchers of All-Russian Scientific Research Institute Of Aviation Materials (Federal State Unitary Enterprise “VIAM”). A setup was developed and manufactured to experimentally substantiate the developed method. Basic unit of the setup is the reactor (Fig. 1) in which the cleaning process of samples installed in a fastening device assembled inside the apparatus is carried out. The apparatus is made of M1 grade copper and supplied with a contact heater. In order to increase the performance index the outer surface of the reactor is coated by the gas-detonation method with titanium oxide ceramics (100 mkm).

In the experiments, the state of the cracks surface of the samples-simulators was controlled by an INCA Energy (X-ray energy dispersion) spectrometer, installed on the LEO-420 focused beam electron microscope. The chosen gas- and hydrodynamics parameters of the process as well as varying temperature (60 to 120°C) and compositions of etching solutions permit removal of metal oxides from narrow gaps (70-120 mkm) during 0.3 – 0.5 h [3].

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PP-III-12

MIXING EFFICIENCY ON PLANT CELL GROWTH AND PROTEINASE PRODUCTION IN A STIRRED TANK REACTOR

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Mixing efficiency is one of the most significant factors in bioprocess productivity. The major role of agitation is to improve broth homogenization, mass and heat transfer inside the bioreactors. The increase of agitation and aeration and a good geometry of the reactor provide better mixing and mass transfer; however, excesses might result in high hydrodynamic stress with negative effects, such as loss of cell viability, rupture of cells, autolysis, changes in membrane integrity, release of intracellular compounds, morphological alterations, variations in intracellular respiration and a decrease in enzymatic production affecting the culture growth [1, 2]. The biomass production and metabolites accumulation in a STR depends on the resistance of the cells to shear stress, balanced with efficient mass transfer and mixing. Impeller design plays a major role in the mixing of fluids and suspensions. Its design influences fluid movement, and in turns the type of liquid involved influences the impeller design. Three-phase mixing, of which cell suspensions are an example, is extremely complex, with heat and gas distribution and solid suspension demanding certain requirements which are heavily influenced by the rheology of the mixture and the levels of shear stress tolerated by the cells. Multiple-impeller systems in the reactor are being applied where shear sensitivity of microorganisms is an important criterion for the process design, due to their efficient gas distribution and lower power consumption per impeller when compared to single-impeller systems [3-5].

Plant cell cultures, due non-Newtonian characteristics and the formation of heterogeneous aggregates, are an important biological model to study cell hydrodynamic stress correlated with oxygen mass transfer rate capacity in stirred tank. Cultures of *Centaurea calcitrapa* cells, presenting aspartic proteinases with milk-clotting activity, were established in a 7 L stirred tank reactor (STR), at initial mass transfer conditions constant (4 h^{-1}). The aim of this work is the understanding of the mixing efficiency on cell growth and proteinase production. In this study were tested two types of impeller, a Rushton impeller and a marine propeller, where the cultures were grown in STR equipped with single or double impellers.

C. calcitrapa cultivated in a STR equipped with two impellers, presented high proteinase activity (235 U/mg DW) and growth, similar to the proteolytic value obtained with single-marine propeller (214 U/mg DW). This system has a very low dissipation energy rate ($\bar{\varepsilon}$), $10x10^{-4}$ W/kg, what may correspond to the higher homogeneity and optimal mixing reached by two-Rushton turbines or by single marine-impeller systems. These results suggest that the mixing efficiency is a key factor for the minimizing shear stress driving the success of a bioprocess in terms of the biomass or the product formation. The choice of the impeller system and mixing conditions were crucial for proteinase and biomass production of *C. calcitrapa* cell suspension.

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PP-III-13

THERMAL EXPLOITATION OF FRUIT TREE PRUNING WASTES IN A NOVEL CONICAL SPOUTED BED COMBUSTOR

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Sweet fruit occupied a surface nearly a million ha in UE in 2002, the main cultivation corresponded to apple tree, 241000 ha, and pear tree, 201300 ha [1]. In Spain the surface occupied by sweet fruit represented the 41.8% with a production of 2420000 ton of wastes The wastes from the pruning of fruit trees has a low-middle humidity content and a high content in cellulose and lignin. Most of these wastes are burnt in the own exploitation after being retired from the land. In Spain the application of these materials to the ground, previous fragmentation and crushed, as a organic wadding of slow decomposition or to superficial incorporation in the ground by means of the suitable farm work as alternative form it is being slowly implanted.

A new technology based in the Spouted Bed gas-solid contact method in conical spouted beds is an alternative easier and more economic (regarding to design, construction and operation) that other solutions such as moving bed dryers, rotary, of trays or of fluidized beds, for energetic valorization, by combustion, of wastes from agricultural activities by reducing the power consumption, not requiring previous milling of sludge and to minimize powder generation.

In previous papers, the operativity of spouted bed technology has been proven for the treatment of coarse and sticky particles [2-3]; with a great particle distribution with low segregation [4] obtaining good results for biomass treatment [5-6], cork wastes [7] and sawdust and wood wastes [8]. In this work, a conical spouted bed reactor has been tuned up for the combustion of vine shoots wastes from Castile lands.

In this paper, a new conical spouted bed combustor for thermal exploitation of wastes of pruning of fruit trees by combustion has been used with homogenous beds wastes of pruning of fruit trees. The combustion of wastes of pruning of fruit trees in a combustor has been carried out in a conical spouted bed combustor in conditions to improve the environment and the evolution of combustion gases has been analyzed. With this aim, the behaviour has been analized by means of hydrodynamic and thermal studies in beds consisting of granular materials.

The experimental unit design for this purpose on a pilot scale, consists of a blower that supplies a maximum air flow rate of 300 Nm^3/h at a pressure of 15 kPa, two high efficiency cyclones in order to collect fine particles, a preheater to heat the gas at the inlet and thermocouples. The flow rate is measured by means of two mass flowmeters in the ranges of 50-300 and 0-100 m^3/h, both being controlled by a computer. The accuracy of this control is $\pm 0.5\%$ of the measured flow rate [9].

Solids used, which correspond basically to the D group of the Geldart classification have been branches of fruit tree grinded to particle diameters of d_p= 25 and 65 mm and their mixtures of $\overline{d_S}$ = 36 mm with moisture of 25 wt % in dry base. The different particles sizes of the branches of fruit trees have been obtained by means of a grinding mill (Fritzch Pulverizette) and have been sieved by means of meshes. The low calorific value of the branches of fruit trees measured with a bomb calorimeter type PARR 1341 with oxygen bomb 1108, digital thermometer 6775 and ignition unit 2901, is 4500 kcal/kg. The stagnant bed height (H_o) values used are in the range of 0.05-0.15 m.

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PP-III-14

KINETIC INVESTIGATION OF PLANT OILS HYDROCRACKING WITH HIGH CETANE BIOFUEL PRODUCTION

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The production of motor fuels from renewable resources has become important due to the exhaustion of fossil resources. Two types of biofuels are most widely used at present: bioethanol and biodiesel produced from sugar and vegetable oils respectively. Besides the biodiesel it may be received another type of biofuel so-called green diesel, or "Supercetane", by hydrocracking triglycerides of fatty acids (palm, soybean, jatropha, canola oils). Green diesel is a mixture of alkane's isomers from C_{12} to C_{18} hydrocarbons. Because of high content of alkanes, green diesel has an excellent cetane number ranging from 55 to 90 [1] and is positioned as improved additive to the traditional diesel.

Usually the production of green diesel takes place in two stages. On the first stage vegetable oils undergoes by hydroprocessing with n-alkanes formation. The second stage is n-alkanes isomerization for improvement of biofuel. Generally, sulfided Ni-Mo [2], Ni-Co, Ni-W supported on the Al_2O_3 are used as catalysts for the first stage. For the second stage bifunctional catalysts, including both the acidic function (zeolites: ZSM-5 [3], ZSM-22, BEA; SiO_2-Al_2O_3 [4]; silica aluminophosphates SAPO-11, SAPO-31 [5], SAPO-41) and the ability of hydrogenation-dehydrogenation (noble metals Pt or Pd), are employed. However, the sulfide catalysts are quickly deactivated because of the low content of sulfur in the feedstock. Therefore the development of non-sulfided catalysts, based on Pt, Pd, Ni, Cu [6], is actual.

In the present work for rapeseed oil hydrocracking were used the following catalytic systems: Ni-Cu/CeO_2-ZrO_2, Ni/SiO_2, Ni-Cu/SiO_2, Ni-P/SiO_2, Ni-Cu-P/SiO_2 and Ni-Cu-Mo/Al_2O_3. The experiments were carried out in a laboratory fixed-bed flow reactor under 360°C, 8,0 MPa (H_2), LHSV= 1, 0 h^{-1}, H_2/oil = 1333 Nm^3/Nm^3, V_{cat}=5 cm^3. Ni-Cu/CeO_2-ZrO_2 catalyst was determined as the most active catalyst. It is worth noting that at mild conditions (300-380°C, 1,0 MPa (H_2), LHSV= 2, 7- 9, 9 h^{-1}) hydrocracking rapeseed oil was not complete with formation of oxygen-containing compounds (free fatty acids and their methyl esters, waxes, ketones, aldehydes, alcohols). Influence of products distribution was studied in dependence on reaction conditions in the presence of Ni-Cu/CeO_2-ZrO_2 catalyst (Fig. 1). The total yield of alkanes was about 60 % wt.

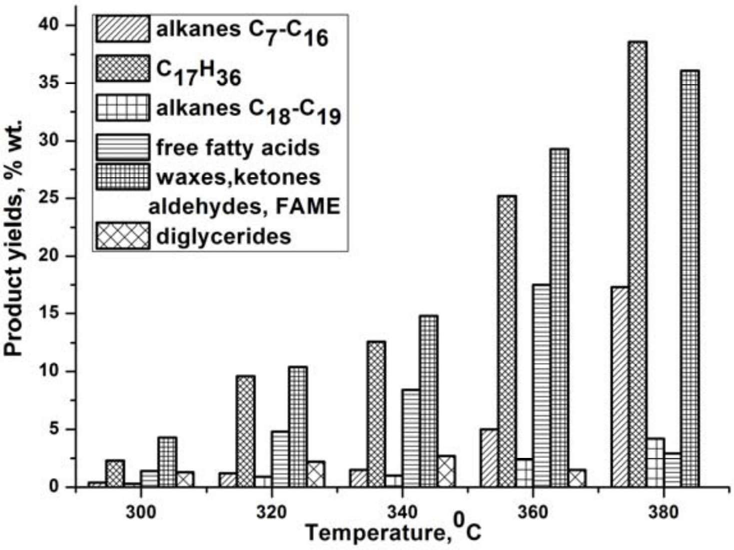

Fig. 1. The dependence of product yields of rapeseed oil on temperature.

The simplified scheme describing the transformation triglycerides of fatty acids was proposed taking into account the formation of intermediate products. This kinetic data will used for process optimization of obtaining green diesel.

Ni-Cu/CeO_2-ZrO_2 catalyst was investigated by different physicochemical methods such as elemental analysis, TPR, TEMHR, XRD, TGA, BET. The TGA analysis showed that the extent of coking this catalyst after reactions was about 3, 3%. It was shown that the presence of Cu in the catalyst Ni-Cu/CeO_2-ZrO_2 allows the NiO to be reduced at lower temperatures.

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CATALYTIC OXIDATIVE DEHYDROGENATION AND CRACKING OF C_3-C_4 ALKANES TO OLEFINS OVER MANGANESE-CONTAINING CATALYSTS

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The direct oxidative catalytic dehydrogenation of C_3-C_4 hydrocarbons to C_2-C_4 olefins offer such advantages as exothermicity of the process, low cost of the feed, and removal of thermodynamic limitations.

The olefin synthesis was carried out in periodic mode. In such conditions the catalyst participated as a reagent, and hydrocarbon conversion occurred with participation of oxygen of the catalyst crystalline lattice. Subsequent reoxidation of the catalyst surface was performed during the oxygen treatment. The manganese-containing systems supported on Al_2O_3 and SiO_2 were used as catalysts. Potassium phosphate was used as a promoter. The specific surface of the catalyst prepared was 119 – 148 °C. Reactor temperature was in the range between 600 and 800 °C. The contact time of the catalyst bed was varied in the range of 0.1 – 0.75 s. Duration of both work and regeneration cycles was 10-15 min.

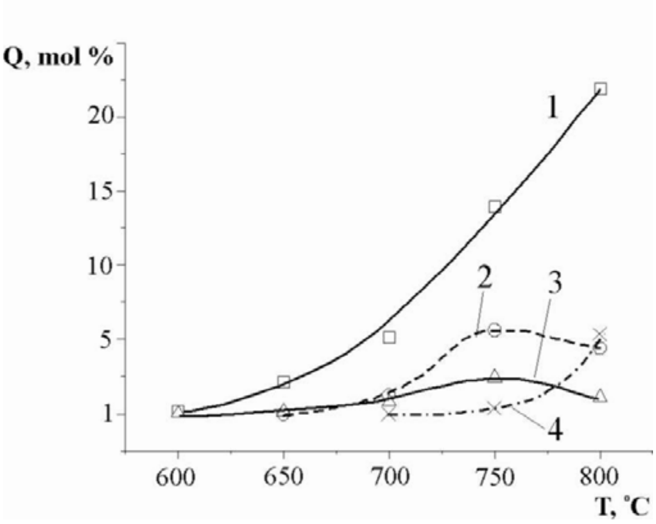

Fig. 1. Dependence of product yields on temperature, catalyst composition was 6 mol.% $Na_3PO_4/MnO_x/Al_2O_3$, the contact time τ = 0,2 c: ethylene (1), propene (2), butenes (3), CO_2 (4).

It was shown that oxicracking reactions occurred on the $MnOx/Al_2O_3$ catalyst.The yield of ethylene, as a C_3-C_4 hydrocarbon cracking product, exceeded those of the dehydrogenation products (such as propene and butene). The yields of total oxidation products (CO_x) were low (Fig. 1).

The high yield of olefins was achieved at low temperature over 2%-Na_3PO_4/17,4%-MnO_x/SiO_2 catalyst. The yields of the dehydrogenation products such as propene and butene was higher in comparison with those for 6 mol. % $Na_3PO_4/MnO_x/\ Al_2O_3$ (Fig. 2).

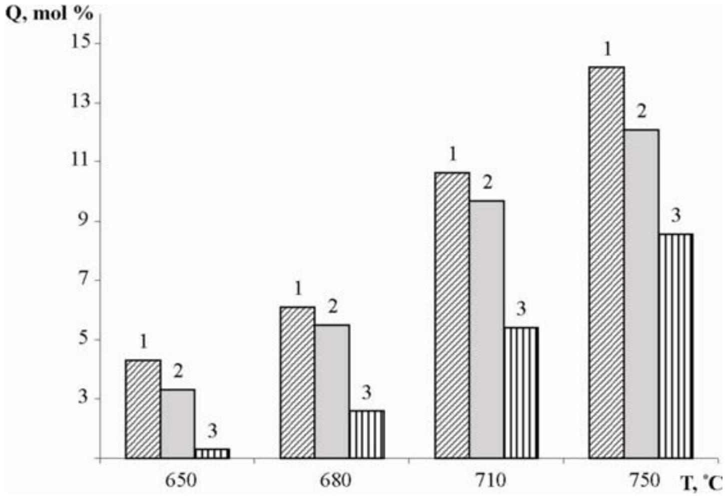

Fig. 2. Dependence of product yields on temperature for the 2%-Na_3PO_4/17,4%-MnO_x/SiO_2 catalyst, the contact time τ = 0,2 c: ethylene (1), propene (2), butenes (3)

Investigation of the influence of an active component loading (MnO_x) on the surface of SiO_2 support had shown that optimal content of manganese oxides on the support was 15-17 %. Increasing in the active component content led to olefin yield reduction because of the rate of total oxidation reactions of hydrocarbons in CO_2 increased. In case of the active component content in catalyst composition was less than 15 %wt, the olefin yield reduced due to low conversion of hydrocarbons.

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CATALYTIC SYNTHESIS OF 2-METHYL-1,4-NAPHTHOQUINONE IN SUPERCRITICAL CARBON DIOXIDE

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Selective oxidation of aromatic compounds opens access to a great number of useful products. Quinones with various functional groups are important intermediate in fine organic synthesis as quininone fragments are part of difficult molecules of the substances used in manufacture of vitamins and medical products. An example of such compounds is 2-methylnaphthalene.

The 2-methylnaphthalene oxidation stage has a low selectivity, and consequently a small target product yield. At oxidation 2-methylnaphthalene such products, as 2-methyl-1,4-naphthquinone (menadione, the precursor of vitamin K3), isomerous 6-methyl-1,4-naphthquinone, methyl groups oxidation products, dinaphthquinone, epoxiquinone and other products of deep oxidation are formed. It necessary to find the way of selective synthesis of menadione. Vitamins of K group, or antihaemorhagic vitamins, are necessary for a normal fibrillation. It s applied at strong bleedings, haemorhagic diathesis and in certain cases of a liver functions frustration. Vikasolum is a sulfosodium derivative of menadione, unlike natural preparations of vitamin K (phytomenadione, etc.) is a water-soluble compound and it can be applied not only inside, but also parenteral.

The growth in interest in supercritical fluids (SCFs) over the past 2 decades results from several key characteristics, which are interesting to both the academic and industrial communities [1]. An SCF is a fluid above its critical temperature and pressure [2]. The factors which have contributed to the interest in SCFs include the environmental problems associated with common industrial solvents (mostly chlorinated hydrocarbons) [3]. The availability of inexpensive, nontoxic SCF solvents such as CO_2 and their attractive properties have renewed interest in the applicability of these solvents. The use of SCF extraction, for example, has been applied to a wide variety of areas, including, most recently, various aspects of environmental control. Supercritical fluids also possess properties that make them attractive as media for chemical reactions. Conducting chemical reactions at supercritical conditions affords opportunities to manipulate the reaction environment (solvent properties) by manipulating the pressure, to enhance the solubilities of reactants and products, to eliminate interphase transport limitations on reaction rates, and to integrate reaction and separation unit operations. Recently, supercritical CO_2 (SC CO_2) has begun to attract attention as an environmentally benign substitute for some halogenated and aromatic solvents used in chemical syntheses.

At first industrial non-catalytic reaction of 2-methylnaphthalene oxidation by a chromic mix has been in vitro researched. Oxidation was conducted in the glass reactor within 10 minutes at the temperature from 40 to 90°C. Concentration of a 2-methylnaphthalene solution in acetic acid is 1M. Samples were taken every 2 minutes during the reaction and analyzed using GC-MS. 2-methylnaphthalene catalytic oxidation was carried out with use of different nanostructured catalytic systems in H_2O_2 presence. As a solvent were used acetic acid and SC CO_2. The yield of the process in acetic acid presence attained only 25%, while the yield of the process in SC CO_2 attained 40%. The further researches will be directed on a variation of parameters of reaction and structure of catalytic systems.

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OXIDATION OF ALKANES INTO OLEFINS ON THE POLYOXIDE CATALYSTS

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Oxidative dehydrogenation of propane-butane mixture (9:1) at Patm into flowing quartz reactor on 0.5-15.0% $H_3PMo_{12}O_{40}$/aluminosilicate catalysts ($S=335m^2/g$) was studied. The investigations were carried out in reaction mixtures of varying compositions containing C_3H_8, C_4H_{10}, N_2, O_2, water vapor. Ratio C_3-C_4-alkanes : H_2O = 1 : 0.21, mol. The influence of temperature, contact time (τ) on oxidative conversion of propane-butane mixture (OCPB), yields (Y), process productivity (P) by C_2H_4, C_3H_6, C_4H_8 were determined.

Formation of C_2-C_4 olefins increases with growth T ≥ 400-800°C. Optimal P by C_2H_4, C_3H_6, C_4H_8 at T = 800°C are (g/l Ct·h): 2748, 1715, 348 (τ = 0.1s), 1437, 1150, 204 (τ = 0.29s), 881, 397, 65 (τ = 0,59s), 468, 263, 40 (τ = 2.0s), accordingly. The yield curves of olefins at decrease of HPA content on the carrier have polyextremal form. There were demonstrated by complex of physical-chemical methods (XRD, IR-spectroscopy and TPR).

The mixture of C_3H_8-C_4H_{10} alkanes of oil gases is utilized as fuel basically. Non catalytic oxidative industrial processes of a synthesis from C_3-C_4-alkanes of sum of the oxygen containing products (aldehydes, ketones, alcohols and acids) are well known. The processes are profitable despite of low selectivity and yields of products. The production of C_2-C_4 olefins, hydrogen by oxidative dehydrogenation of C_3-C_4 alkanes is interesting, as yield and selectivity of C_2H_4, C_3H_6, and C_4H_8 in well known oxidative dimerization (OD) of CH_4, C_2H_6, C_3H_8, C_4H_{10} and processes are low. The using of the mixture of hydrocarbons allows to intensive the processes.

The influence of T, τ on oxidative conversion of propane-butane mixture (9:1) at Patm on 0.5-15.0 % $H_3PMo_{12}O_{40}$/aluminosilicate was studied. The investigations were carried out in a flowing quartz reactor with the fixed layer of catalyst in the reaction mixtures of varying compositions containing C_3H_8, n-, i- C_4H_{10}, O_2, N_2, water vapor. Ratio C_3H_8-C_4H_{10} : H_2O = 1 : 0.21, mol., T = 200-800^{0}C, τ = 0.1-2.0 s.

A negligible sum of oxygen-containing products (aldehydes, alcohols, C_1-C_4 acids, Σ Y = 1-6%) was generated at T = 100-400°C in spite of variation of experimental conditions in

OCPB process. The OD productions and cracking products at deficiency of oxidant (CH_4, H_2, CO_2) are generated simultaneously at T=300-800°C.

The yield curves of C_3H_6 and CH_4 ($\tau = 1.2$ s), C_2H_4, CH_4, H_2 ($\tau = 0.29$s) were practically combined. It is proposed that two process of oxidative conversion of C_3, C_4-alkanes : OD with the formation of C_2H_4, C_3H_6, C_4H_8, H_2 and cracking of initial alkanes with the formation of CH_4, C_2H_4, C_3H_6 (was intensive at conversion of $O_2 \sim 100$ %) are carried out at T = 600-800°C.

Results the influence of contact time, temperature on yield and productivity of C_2-C_4 olefins formation in OCPB on 15% $H_3PMo_{12}O_{40}$/AlSi indicate on the growth of these values with increase of T (600-800°C) and τ (0.1-2.0). The productivity of C_2H_4, C_3H_6, C_4H_8 at T = 800°C are (g/l Ct·h): 2748, 1715, 348 ($\tau = 0.1$ s), 1437, 1150, 204 ($\tau = 0.29$ s), 881, 397, 65 ($\tau = 0.59$ s), 468, 263, 40 ($\tau = 2.0$ s), accordingly. The yields of olefins (C_2H_4, C_3H_6, C_4H_8) are changed at variation of the ratio C_3-C_4 alkanes : O_2 from 1:1 to 25:1, vol. Optimal yields (15, 12 and 14% at T = 800°C and $\tau = 0.29$ s) were found at ratio 2.9:1.

The yield curves of olefins at varying of HPA $H_3PMo_{12}O_{40}$ content on aluminosilicate (0.5 - 15%) have polyextreme character. The maximum values of Y and P from C_3H_8-C_4H_{10} mixture are observed on 1.5 and 10% catalysts (C_2H_4); 0.5, 5, 10, 15 % HPA (C_3H_6), 0.5, 3.5, 15 % HPA (C_4H_8). Maximal Y and P of the olefins: C_2H_4 -48.6 %, 184 kg / kg·HPA·h on 1.5% catalyst, C_3H_6 25%, 97.8 kg / kg·HPA·h on 1.5% catalyst, C_4H_8 14%; 13.6 kg / kg·HPA·h on 15% catalyst.

By complex of physical-chemical methods (XRD, IR-spectroscopy, TPR) was shown, that the polyextreme alteration from contents of HPA on carries are caused by mutual influence of components in system “HPA-support” due to superfine distribution of HPA on carrier with formation both crystallites and finely dispersed phase interacting with aluminosilicate.

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PP-III-18

DEEP OXIDATION OF TOLUENE ON POLY-OXIDE NICKEL-COPPER-CHROMIUM CATALYST

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At present the problem of ecological protection of the environment from emissions of industrial enterprises, i.e. chemical safety becoming increasingly important.

Toluene, xylene, styrene, butyl acetate, isobutanol, formaldehyde, acetone, ethanol, etc., which have a strong toxic effect on living organisms, are among the main harmful emissions from industrial facilities (furniture shop, paint production, cable plant, the production of pharmaceuticals, printing venture, etc.).

Toluene, xylene and ethyl benzene are major part of the solvents that are used in various industries and presented in the gas emissions. At present it is known that the catalytic method is the most effective way to neutralize. In this regard, the development of efficient catalysts in deep oxidation of organic harmful substances is an urgent problem of ecology.

Toluene as the main component of emission of furniture, cable, footwear and other industries we have chosen as a model substance.

The catalysts were prepared by capillary impregnation of mixed aqueous solutions of nitrate salts of metals on aluminum oxide on its moisture content, followed by drying at 453-473K (4-5 h) and calcination at 873K (1.5 h) in air [1]. Granular θ-Al_2O_3 ($S = 100 m^2/g$), modified by 2% Ce was used as a carrier. As a result of heat treatment the surface perovskite $CeAlO_3$, stable up to 1373K, was formed.

The content of the initial reactants and reaction products were determined at the "Crystal 2000M" chromatograph with a flame ionization detector with a capillary column 50 m long.

The catalytic activity of the catalysts was determined in a flow installation in the deep oxidation of toluene in air at different temperatures (523-773K), space velocity ($5\text{-}15 \times 10^3\ h^{-1}$) and the concentration of toluene (320 mg/m^3) in the initial mixture of air.

In studying the effect of process parameters (temperature, space velocity, the concentration of toluene in the gas mixture) to complete conversion of toluene (to CO_2 and

H_2O) showed that the synthesized polyoxide Ni-Cu-Cr catalyst supported on a 2% Ce/θ-Al_2O_3 in the oxidation of toluene at a space velocity 5×10^3 h^{-1}, a temperature of 723-773K and the content of toluene in the mixture 100 - 570 mg/m^3 provides 98.8% conversion of toluene to CO_2 [2-3].

The synthesized Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalysts have been investigated by X-ray analysis (XRD) and transmission electron microscopy (EM).

Phase composition of catalysts was determined by X-ray diffractometer DRON-4-7, Co-anode, 25kV, 25mA, 2θ-5-80° C. According to the XRD during the synthesis of catalyst after heating at 873K on the surface of carrier reported the presence of crystals CeO_2 and X-ray amorphous clusters (d = 20-100Å) of variable valence metal oxides NiO, CuO as well as solid solutions of metals CuO(NiO). With the heating of Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst occurs not only the crystallization of CeO_2, but also sharply increases the content of α-Al_2O_3, starting with 1273K. A significant decrease in the total surface area of catalysts occurs as heating due to this process.

The morphology, particle size, chemical composition of Ni-Cu-Cr catalysts have been investigated using a transmission electron microscope EM-125K with an increase by 80 000 replicas with extraction using micro-diffraction with an increase in the catalyst component. It was found that in the process of complexity of composition of Ni-Cu-Cr catalysts produced single, double, triple metal oxides, the particle size of which decreases from 50-80 (Ce/Al_2O_3) up to 20-30Å (Ni-Cu-Cr).

Thus has been developed the polyoxide Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst with desired properties on the carriers for deep oxidation (to CO_2 and H_2O) of hydrocarbons - toluene, xylene, styrene, ethyl acetate, butyl acetate, isobutanol, formaldehyde, acetone, ethanol and others who have a strong toxic effect on living organisms and flora.

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CATALYTIC CONVERSION OF ASSOCIATED PETROLEUM GAS INTO METHANE-HYDROGEN GAS MIXTURES. ECONOMIC BENEFITS FOR USING WITH ICE- AND SOFC–BASED POWER GENERATION UNITS

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Development of new oil-field territories of Arctic shelf stimulates researches for new technologies of associated petroleum gas (APG) utilization. APG is a high-caloric gas of variable composition consisting of methane, ethane, LPG, nitrogen, carbon dioxide and some other components such as sulfuric compounds, helium, argon. Because of relatively high content of non-methane fraction, APG could not be pumped directly into gas pipelines especially at low temperature conditions of Russian North territories. Since oil fields in Russian North and Arctic shelf locates far away from industrial centers and cities where construction of transportation infrastructure comes highly expensive, the APG utilization approaches are focused mainly on generation of electric power, which can be used both for local needs and transported for long distances. Direct use of APG as a mono-fuel for power generation (gas engines, gas turbines) is limited by low methane content, unstable gas composition and high coking risk that decreases service life and causes engine damage. To overcome these problems, technology of preliminary catalytic steam reforming of APG hydrocarbon components to produce methane-hydrogen mixture is proposed, which can be used for power generation applications.

When the power generation unit based on internal combustion engine was fuelled by methane-hydrogen mixture produced by APG catalytic reforming, the engine attained the nominal characteristics. The produced methane-hydrogen mixture can also be used for feeding solid oxide fuel cell power generation unit.

Commercial feasibility of the technology depends on whether the APG resource is industrially significant or unprofitable. Criterion for resource attributing to a certain type is based on economic efficiency factor of capital investments to the system of APG utilization. For each oil field with a specific debit and gas composition, effective technology of APG utilization should be selected to make capital investments economically beneficial.

Comparative analysis of economic efficiency and commercial feasibility of the proposed technology was performed for a number of power generating units fuelled by methane-hydrogen mixture generated in the APG reformer, and similar power units fuelled by initial APG. It was analyzed also how the payback period of APG-fuelled power generating units depends on such key parameters as decreased service life, short time between overhaul and rated power loss.

Calculations conducted for different types of power plants with electrical power of ~ 1000 kW (for example, based on Perkins (Great Britain), Waukesha (USA), Deutz (Germany) gas internal combustion engines) show that recoupment of capital investment is significantly faster for power plants equipped with catalytic reformer of APG into methane-hydrogen mixture as compared to APG-fed power plants. This is achieved by extended service life of the power plants, longer time between overhaul services, nominal power characteristics.

In this work, feasibility of commercial application of catalytically converted APG for feeding solid oxide fuel cell power generation units with different electric power outputs were also anylised.

Acknowledgements

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VIRTUAL PARTICIPATION

RESEARCH PROCESS GAS-PHASE OXIDATION OF METHANOL ON THE MODIFIED ZEOLITE ON A PILOT PLANT

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Over the years, the Institute of Chemical Problems conducted original research on the study of gas-phase oxidation of aliphatic alcohols on modified natural zeolites. The distinctive features of the studied process are high yields of desired products with high selectivity and simplicity of their design process, creating good prospects for the widespread introduction of these processes in industry.

One such reaction is the process of gas-phase oxidation of methanol in formic acid on Pd^{+2}- containing zeolite catalyst. According to laboratory research has been developed kinetic model of the process /1/. Its value is confirmed by statistical analysis models and formulation of discriminating experiments in a laboratory setting. The volume of the reaction zone in the used reactor was 6 cm^3. To estimate the resulting model in the case of reactors, a large amount of further experimental investigation of the process were carried out on an automated test facility, which is conjugate to a personal computer (PC) and containing a metal reactor of 250 cm^3.

In view of these laboratory studies on the first stage of the experiments were set to find the optimal region of the process. At this stage, was used developed software that implements various algorithms for optimal design of experiments. Experiments were carried out at atmospheric pressure in a stationary field of activity of the catalyst. As a managed set of parameters was chosen: reactor temperature - T, the feed rate of methanol V_{CH_3OH}, oxygen V_{O_2}, nitrogen V_{N_2}, the molar ratio of methanol: oxygen: nitrogen. To study the zero-point levels and ranges of variation of controlled parameters were assumed to be respectively

$$350 \le T \le 420\,K; \quad 900 \le V \le 3200\,h^{-1}; \quad 0{,}13 \le P_{0_2} \le 0{,}6\,atm; \quad 0{,}09 \le P_{CH_3OH} \le 0{,}43\,atm,$$

$CH_3OH:O_2:N_2$ – 1:1:2, where P_{0_2} and P_{CH_3OH} - the partial pressure of oxygen and formic acid, respectively.

The experiments were set and held in accordance with the selected rotatable central composite plan /2/. After they were introduced in the PC of the value of the response function of W - the value of the rate of formation of formic acid, using data from chromatographic analyzes of reaction products. The optimal value of the rate of formation of formic acid, 45.5% achieved at a temperature of 383 K, molar ratio of methanol: oxygen: nitrogen - 1:1:2. Control experiments found values in the set of controlled parameters that lead to the largest $W_{F.A.}$ - located in close agreement with data optimization.

In the field of the found optimum of the process raised a number of experiments using different sizes of granules of the catalyst system. The experiments were performed with the following dimensions of the catalyst granules: 0,25-0,63 mm. The results showed that the rate of formation of formic acid with a change in the granule size of the catalyst does not change. This indicates a lack of influence of internal- diffusion factors on the rate process.

To determine the influence of external- diffusion factors on the rate of the process, experiments were conducted under optimal conditions with different bulk velocities of the reaction. It was found that the change of its velocity in the range of 850-3100 h^{-1} does not affect the rate of formation of the desired product. The latter indicates that the process does not influence external- diffuzion factors.

Studies have been conducted in the kinetics of wide ranges of variation of control parameters of the pilot plant.

The nature of the dependency rate of $W_{F.A.}$, selectivity, S, and X conversion process from controlled parameters similar to the analogous dependences obtained in a laboratory setting and is well described theoretically.

The discrepancies between the experimental and theoretical dependences found do not exceed 6%, which confirms the adequacy of the developed kinetic model and the use larger volume reactors.

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RICE HUSK VALORIZATION BY FAST PYROLYSIS IN A CONICAL SPOUTED BED REACTOR

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Rice husk is an agricultural waste material abundantly available in rice-producing countries. Traditional methods as composting and incineration are not suitable to process these organic solid wastes as they contain small concentrations of nitrogen for composting and a considerable amount of ash for their combustion [1]. They are favourable feedstock for pyrolysis because of their steady supply form rice plants and proper physical properties for providing bio-oil. As the main objective is to maximize the liquid yield, the best choice is a fast pyrolysis process where the feedstock is rapidly heated in the absence of air to obtain high yields of bio-oil [2]. In this study, the fast pyrolysis of rice husk was investigated in a conical spouted bed reactor.

The spouted bed reactor consists of a lower conical section and an upper cylindrical section. The design has been based on the extensive knowledge acquired in previous studies in the pyrolysis of other waste materials such as waste tires, plastics and other types of biomass [3,4]. The bed was initially made up of 100 g of sand, allowing the continuous removal of the char from the bed by a lateral outlet, which avoids its accumulation throughout the pyrolysis process. Nitrogen has been used as fluidizing agent, and it is heated to the reaction temperature by means of a preheater.

The products obtained in the fast pyrolysis of biomass have been grouped into three different fractions: gas, bio-oil and char. As water content in the bio-oil is considerable, the evolution of its yield with the temperature is also displayed. The results of the obtained yields are summarized in Table 1. The bio-oil yield was maximized at 450 °C, but then decrease with increasing the temperature. When the temperature increases, occur the secondary cracking of the pyrolysis vapours and bio-oil and char yields decrease while the gas yield increases.

The gas fraction is mainly made up of carbon monoxide and carbon dioxide, whose yields increase with the temperature. As it can be observed in Figure 1a, CO_2 concentration in the gaseous fraction decreases when the temperature increases, whereas that of CO increases. This is because descarboxylation reactions becomes more important at higher temperatures than those of decarbonylation. The yield of C_1-C_4 hydrocarbon and hydrogen increases with temperature due to the secondary cracking of volatiles.

Table 1. Effect of temperature on product yields in rice husk pyrolysis (on wet basis).

Yield (%wt)	400 °C	450 °C	500 °C	600 °C
Gas	1,1	4,0	5,8	8,8
Bio-oil	67,3	70,5	69,0	67,2
Water	23,7	22,8	23,0	23,6
Char	31,6	25,5	25,2	24,0

In view of results presented in Figure 1b, it could be seen that the major compounds in the bio-oil were phenolics and ketones. The presence of acids, sugars and aldehydes are due to the carbohydrate fraction of the rice husk (cellulose and hemicelluloses), while phenolic compounds and ketones are derived from the lignin fraction.

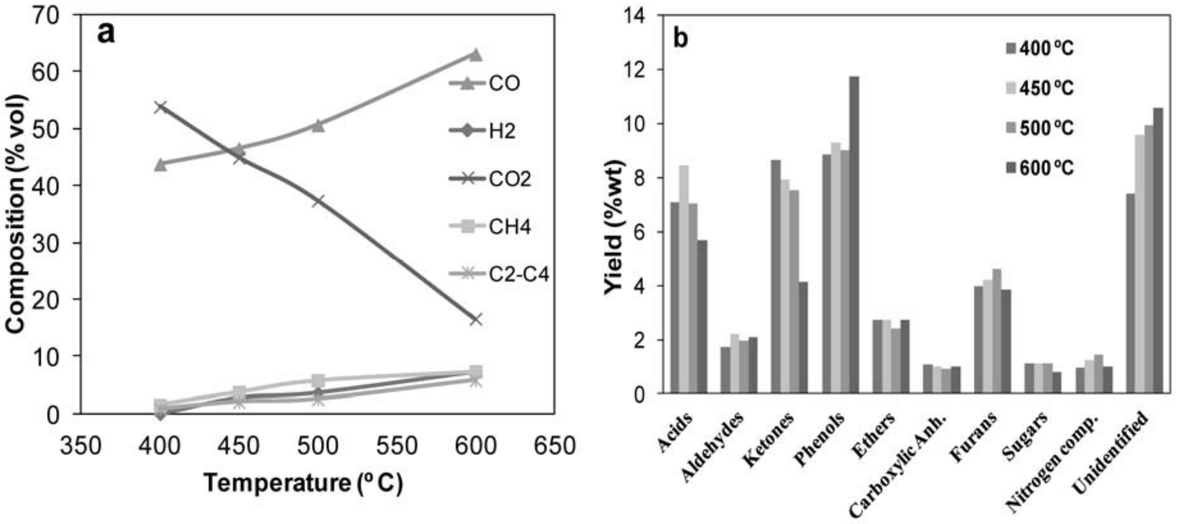

Figure 1. a) Influence of temperature on gas composition.
b) Yields of main chemical groups of bio-oil at different temperatures.

As shown in Table1, the gas yield is really low, especially when it is compared with other results from rice husk fast pyrolysis [5]. Using a spouted bed reactor is possible to reduce the residence time and improve the gas-particle contact. Consequently, secondary reactions are minimised and the bio-oil yield is considerably improved.

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HONEYCOMB MONOLITHIC CATALYST REACTORS FOR SPACE PROPULSION APPLICATIONS

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The pellet and the grain catalysts have been widely used in space propulsion applications, such as launcher, satellites and gas generator (e.g. rescue systems) [1, 2]. The use of monolith in these applications is only at the development stage. However, compared to conventional catalysts shape (e.g. pellets, spheres, grains), monolithic catalysts have several advantages such as (i) low pressure drop, (ii) possibility of using high flow rate, (iii) easiness in scale-up and in some cases (iv) selectivity enhancement. Nevertheless, this type of materials presents a very low surface area, and therefore needs the deposition of a secondary porous support in the form of a washcoat layer.

In our laboratory we are also interested by the development of the wash-coating phase in order to increase the surface area of the monolithic support and therefore the metallic active phase(s). In the present work, honeycomb-based catalysts have been manufactured from ceramic monoliths containing porous γ-alumina as a secondary support. This later has been prepared from boehmite colloidal suspension and urea, and deposited onto the internal surface of the monolith. The active phase components are based on precious metals (Pt, Ir or Rh) or transition metal oxides such as MnO_2 [3].

To follow the catalytic activity, cordierite-based honeycomb catalysts ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) (Figure 1) were evaluated for the decomposition of energetic compounds such as hydrogen peroxide, hydroxylammonium nitrate, ammonium dinitramide, ignition of cold $H_2 + O_2$ mixtures, …

Fig 1. The as-received monoliths (1 cm in diameter) (a) and the catalysts after wash-coating by porous alumina and impregnation by iridium (b).

The control of the catalytic bed and the different preparation key parameters of the catalysts remain an important way to improve the catalytic decomposition and the catalytic ignition performances: (i) honeycomb-type ceramic monoliths, (ii) wash-coating procedure, (iii) impregnation steps: the active phase is deposited inside the porosity of the coating layer by impregnation of the active phase precursor followed by drying, calcination and/or reduction. The monolithic catalysts based on the noble metals are characterized by different physico-chemical techniques to understand their behavior.

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MICROREACTORS FOR SPACE PROPULSION APPLICATIONS: FOAM CATALYSTS

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Open-cell ceramic foams on cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) and silice carbide (SiC) with pore counts between 20 and 30 PPI (Pores Per Inch) (Figure 1) were studied in connection with their morphology have gained interest in the last decade due to their potential applications as carriers in various processes. Their properties such as low pressure drop, high surface area enhancing mass transport, as well as the radial mixing in the tortuous structure, improving heat transfer in highly endothermic and exothermic reactions, make them attractive in many research fields. They have already been used in several applications such as waste and exhaust gas purification [1, 2, 3], methane and propane combustion, carbon dioxide reforming, partial oxidation of hydrocarbons at short contact times, preferential oxidation of carbon monoxide in hydrogen and Fischer–Tropsch-synthesis [4]. Most of these applications involve high flow rates and/or high reaction rates, typically controlled by external mass and heat transfer. The knowledge of mass (and heat) transfer and pressure drop properties of these reticulated structures is therefore of extreme importance for reactor design and industrial implementation.

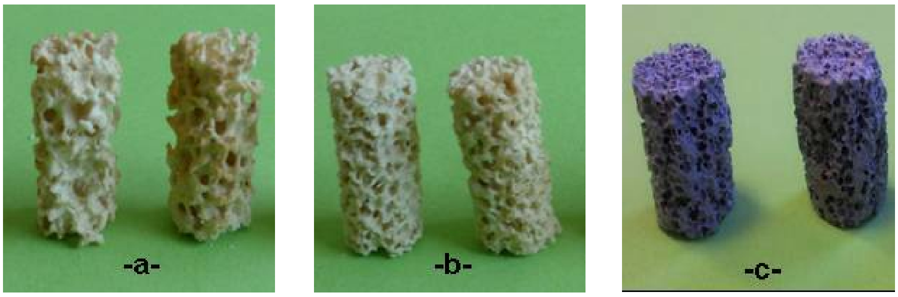

Figure 1: The received monolith foams (9 mm in diameter and 20 mm in lenght), cordierite 20 ppi (a), 30 ppi (b) and silice carbide 30 ppi (c).

The focus of this work is therefore to prepare the monolithic faom catalysts based on noble metals (Ir, Pt, Rh and Ir) for ignition of cold H_2/O_2 mixtures. The prepared monolith faom catalysts are characterized by physico-chemical techniques (X-ray diffraction, Scanning electron microscopy, nitrogen physisorption, …etc).

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NEW MICROREACTOR FOR H_2/O_2 CATALYTIC IGNITION FOR SPACE PROPULSION APPLICATIONS

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The catalytic ignition of cold hydrogen-oxygen mixture rich on hydrogen flow rate is known since the early XIXth century and the first kinetic studies by Boreskov et al. have shown a surface chain mechanism [1,2]; metals of the column 10 of the periodic table such as Ni, Pd, Pt display the best activities. The first studies on catalytic ignition of cryogenic mixtures appeared in the sixties in the USA, in relation with the development of the Shell 405 catalyst for hydrazine decomposition. Several industrial catalysts have been evaluated with good activity [3]; a minimum flow rate is necessary to avoid pressure spikes. The catalysts are in pellet shape and the combustion chamber diameter/pellet size ratio of the catalyst bed must be high to limit boundary effects. The best catalysts are Rh-Pt/Al_2O_3 (Engelhard) and Ir/Al_2O_3 (Shell 405) [4]. Experiments carried out on the full-scale test bench of Air Liquide Company demonstrated the catalytic ignition of O_2/H_2 bipropellant mixtures at low temperature (180 K). Catalyst supports selected for this study are cylindrical monoliths: cordierite and mullite honeycomb (100-400 channels per square inch) manufactured by CTI Company (Salindres, France). These materials are coated by porous γ-alumina to increase their specific surface area, and then impregnated by different noble metals precursors and finally thermally treated under reductive atmosphere: the noble metals are: platinum, iridium, rhodium and iridium-rhodium. The monolithic catalysts based on the noble metals are characterized by different physico-chemical techniques before and after catalytic tests to understand their behavior and possible transformation. In parallel, a microreactor (Fig. 1) was conducted at the laboratory of catalysis in organic chemistry (LACCO) to study the catalytic ignition of hydrogen-oxygen bipropellants using a premixing hydrogen oxygen injection.

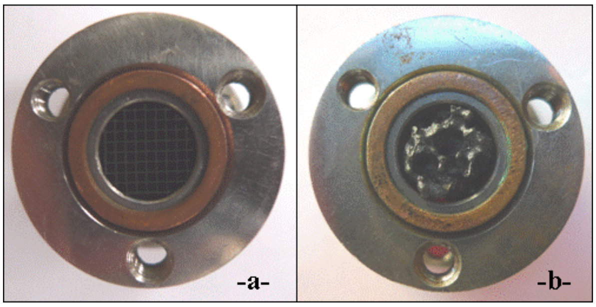

Fig. 1. Internal sections of microreactor in the presence of monolithic iridium-based catalyst (a) and in the presence of the foam iridium-based catalyst (b).

The microreactor was mounted in a building well under pressure and secures using the mechanical workshop under the 13th CPER-Transport (Contrats-Projets-Etat-Région) in the field of space propulsion applications. A laboratory-scale test microreactor is developed in order to reduce the cost of the evaluation tests as well as the catalyst mass (by two orders of magnitude) of the needed catalysts necessary to expand the experiment parameter matrix and to determine the kinetic parameters at room temperatures in the first time and at low temperature in the second step. The microreactor leads to initiate catalytically the ignition of cryogenic H_2/O_2 mixtures cooled by a regulated cryogenic thermostat and special non-flammable oil able to cool the gas flow up to 180 K. To avoid too large heat transfers, the microreactor itself will also be cooled with liquid nitrogen or by the bath oil, and insulated with glass wool.

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DYNAMIC REACTOR FOR SPACE PROPULSION: INSTALLATION AND FIRST RESULTS

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Space missions use neat hydrazine with an iridium catalyst in monopropellant applications, mainly for orbit and attitude control of satellites. Unfortunately, hydrazine-based propellants are considered extremely toxic and its replacement by less toxic propellants is of current interest to reduce the additional costs linked to this toxicity. Among possible hydrazine substitutes, aqueous energetic ionic liquids comprising an ionic oxidizer, an ionic or molecular fuel, and water as solvent, are often proposed and investigated as new monopropellants [1,2]. The oxidizer can be HAN (hydroxylammonium nitrate), ADN (ammonium dinitramide) and AN (ammonium nitrate) or more generally any combination of reductive cation (NH_3OH^+, $N_2H_5^+$ and NH_4^+) and oxidizing anion (NO_3^-) sufficiently soluble and stable in aqueous solution and displays good material compatibility. The oxygen balance of the ionic solute remains always positive; therefore, a fuel needs to be added to improve the performances. The fuel (or reducer) can be ionic (i.e. ammonium or hydrazinium azide, etc.) or molecular (alcohol, glycerol, ether, amino-acid, etc.). One of the advantages of ionic fuels over molecules species is to increase the oxidizer solubility [3].

In previous work, A dynamic reactor coupled with mass spectroscopy online product analysis (cf. Fig. 1) has been used to study the thermal and catalytic decompositions of ionic liquid propellants. The activity of different catalysts has been evaluated by determining qualitatively and quantitatively the reaction products.

V-6

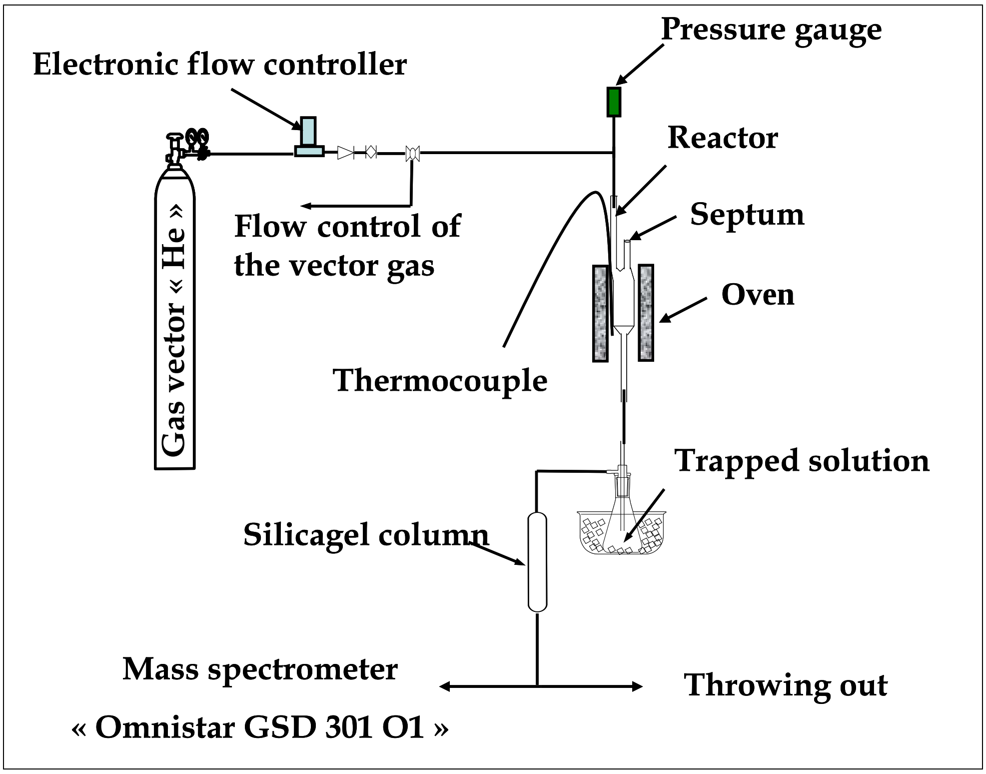

Fig. 1. Design of dynamic reactor coupled with mass spectrometer.

The thermal and catalytic decomposition of binary HAN-water (86 wt. %) and binary AND-water (50 wt. %) mixtures gave primary products (major N_2, medium NO) and secondary products (medium N_2O and traces NO_2). From the data, a reaction mass balance could be proposed, based on the combination of two parallel competitive reactions:

- $6\ NH_3OHNO_3(aq) \rightarrow 3\ N_2(g) + 2\ NO(g) + 10\ H_2O(g) + 4\ HNO_3(g)$, $\Delta_r H = -117.8$ kJ mol^{-1}
- $6\ NH_3OHNO_3(aq) \rightarrow 2\ N_2(g) + 2\ N_2O(g) + 10\ H_2O(g) + 4\ HNO_3(g)$, $\Delta_r H = -121.0$ kJ mol^{-1}

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LIQUID PROPELLANTS DECOMPOSITION USING DYNAMIC REACTOR: REACTION BALANCES

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The laboratory of catalysis at Poitiers University has been working for about 10 years on the use of nitrogen-based ionic monopropellants as possible hydrazine substitutes or as new propellants [1,2,3,4,5]. Indeed, we presented the first results concerning the complete reaction mass balance of thermal and catalytic decomposition of HAN-based propellants using the dynamic reactor [6]. The decomposition of HAN-water solution (HAN 80 wt.-%) gave for the gas phase, major nitrogen N_2 (thermodynamic product) and medium nitric oxide NO (kinetic product) as primary products; secondary products are medium nitrous oxide N_2O and traces nitrogen dioxide NO_2. The second expected primary product O_2 was not observed. The presence of trapped nitric acid and the formation of solid ammonium nitrate downstream were evidenced. Thus, the delayed formation of nitrous oxide was linked to the intermediate formation of ammonium nitrate. From these data, a reaction mass balance could be proposed, based on the combination of two parallel competitive reactions. The most important result is that nitric acid is a major kinetic product that could not be detected by mass spectrometry, but was qualitatively evidenced by Raman spectroscopy. Thermodynamic and equilibrium calculations for HAN decomposition show that the formation of nitric acid as major product leads to the highest energy release.

Most of the open literature data concern the thermal decomposition of HAN-based monopropellants. Mechanistic studies focused mainly on the use of spectroscopic techniques to identify transient species formed during the first stages of the decomposition. The balanced equations of the decomposition reaction were the subject of few papers using generally infrared absorption or Raman scattering spectroscopy to quantify the product formation. The different results disagree, due to the lack of active infrared vibration bands for dinitrogen species.

In this work, we present the first results concerning the mass balance for the decomposition of other oxidizer candidates: ADN [7], HNF [8] and AN. This will lead to the first full comparison between the different oxidizers and to the related selectivity of the decomposition reactions, i.e. the formation of the kinetic products versus the thermodynamic products. Another key parameter is the relationship between decomposition selectivity and ignition procedure: thermal or catalytic.

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COLLAPSING MICROBUBBLES ARE CHEMICAL MICROREACTORS

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Useful properties of cavitation in liquid are widely studied regarding their application to chemistry, in particular, in environmental chemistry: in water purification from organic impurities.

The nature of cavitation can be acoustic arising upon a propagation of ultrasonic waves in fluid and hydrodynamic occurring in turbulent flows in times of discontinuity of fluid medium. It was noted that an efficiency factor of devices of hydrodynamic (bubble or jet) cavitation is significantly higher (up to 75%) than in devices with ultrasound, the most studied, technique of generating cavitation [1, 2]. The hydrodynamic technique of the generating cavitation is of the most interest due to low equipment cost and a scaling simplicity [1, 3]. Application of cavitation in combined treatment methods is especially efficient with an ultraviolet light, hydrogen peroxide, ozone, and Fenton's reagent [3 - 8].

It is known that inside of collapsing cavitation bubbles there arises great pressure and develops temperature up to 5000 K. Under such conditions cavitation is accompanied by H_2O decomposition and formation of H_2O_2, OH, and H radicals [2, 9 - 11]. Cavitation activates also gases dissolved in water, in particular, an oxygen activation leads to formation peroxiradicals and hydrogen peroxide [12].

The collapsing bubbles can be considered as chemical microreactors where under extreme conditions occurs activation of various physicochemical processes and arise conditions for proceeding of many red/ox reactions that do not occur under normal conditions.

Here we studied processes proceeding in aqueous solutions in the case of low pressure hydrodynamic cavitation.

Examinations were conducted on an experimental setup with thermostatic control. This setup consisted of an averager, cavitation chamber, and vertical multistage centrifugal pump Grundfos CRNE1-15 equipped with a frequency converter. The experiments were carried out in a circulation mode (the volume of treated solution 8 1) at a pressure of the hydrodynamic flow 5±0.25 atm and constant temperature of 20°C. A nozzle with a diameter of 4 mm inlet, placed in a cavitation chamber we used as a generator of hydrodynamic cavitation. For a detailed understanding of the nature of the phenomena occurring in the cavitation chamber we carried out computer simulations using a fluid dynamics software package Flow-3D.

A strong oxidizer, OH radical, plays a special role in the cavitation. The high reactivity of hydroxyl radicals determines their low steady-state concentration in the solution and, therefore, significant difficulties in their detection. Use of hydrophobic or highly volatile compounds as chemical dosimeters allows solving this problem. In this case, the interaction of hydroxyl radicals and the dosimeter occurs inside the bubble or at the interface gas-liquid. As a dosimeter in the further experiments we selected benzene. Changes in the absorption spectra of benzene before and after cavitation impact and also results of quantitative analysis clearly point to the formation of phenol. After 60 min treatment the phenol concentration was 10 μmol l^{-1}.

At the same time, the intensity of cavitation impact and, as a consequence, an amount of hydroxyl radicals formed largely depend on structural features of the generators and plants.

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HYBRID CARBON-BASED NANOSTRUCTURES FOR EMERGING APPLICATIONS

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Hybrid materials consisting of graphitic nanostructures (carbon nanotubes (CNTs) and graphene) and various metal nanoparticles have been widely studied as functional components in catalysis and fuel cell applications [1,2]. Thus, graphene-based structures are used as the scaffold material for metal particle deposition, due to their extraordinary properties, such as large specific surface area and light mass density. The deposited metal species cover a wide range of speciation and functionality, whereas the compounding approaches involve photo-induced reduction of metal precursors, reduction in hydrogen atmosphere, polyol-based process, chemical grafting, hydrothermal methods and physical deposition [3]. Homogeneous deposition and high dispersion of precious metal nanoparticles is desired in order to improve their catalytic activity in processes with high energy and environmental impact. Few studies have been conducted on the catalytic activity of hybrid nanostructures consisting of graphitic nanostructures and Pt-based nanoparticles, focusing on the conversion of CO into CO_2 [2,4]. Concerning the study of hybrid stuctures based on Au nanoparticles, there are no detailed studies in the literature. The Pt/CNT catalyst exhibits a superior performance in terms of catalytic activity and selectivity towards CO_2 formation as compared with Pt/AC catalyst [4]. CeO_2 addition promotes both catalytic activity and selectivity at low temperatures (CO conversion rate of 46% at 313 K), resulting in a superior catalytic performance as compared with a conventional Pt/CeO_2 catalyst. In the present work metal nanoparticles of Pt or/and Au are deposited on carbon nanostructures, such as carbon nanotubes and graphene, via a hydrothermal procedure. (Preferential) CO oxidation is employed as a probe reaction to study the performance of these materials.

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V-10

RECENT ADVANCES IN THE DEVELOPMENT OF INTERNAL REFORMING METHANOL FUEL CELLS

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The remarkable recent advances in wireless and portable communications devices have fueled the need for high-energy-density portable power sources. The low energy densities of current battery systems contribute to the excessive weight and bulk of portable equipment, and severely limit the duration of military operations using portable electronic devices. As a result, several options for higher-energy-density power supplies have been put forth. The low energy densities of current battery systems contribute to the excessive weight and bulk of portable equipment, and severely limit the duration of military operations using portable electronic devices. As a result, several options for higher-energy-density power supplies have been put forth.

Reformed methanol fuel cell (RMFC) is a type of indirect methanol fuel cell, which first converts methanol into hydrogen with a methanol reformer; and then the hydrogen rich gas is sent to a hydrogen/air fuel cell to generate electricity. The process of methanol reforming must be carried out at 250 – 300°C in order to obtain more than 90% fuel conversion efficiency and 50% hydrogen concentration. However, the state of art H_2/air fuel cell in the RMFC can work only between 160-180°C. There is a mismatch of the operating temperatures between the fuel cell and the reformer. In addition, there are two subsystems in a common RMFC, where the reformer and the fuel cell are located separately. Therefore, many auxiliary components are needed for each of the subsystems. If only one or two components have a problem, the whole RMFC will not work. Furthermore, these components not only consume additional power and energy, but also increase the total system weight. Only about 40-50% energy efficiency can be obtained by reforming methanol to hydrogen, and about 50-60% of this energy can be converted from the hydrogen rich gas to electricity in the fuel cell. Therefore, the final energy efficiency is less than 30% in a traditional RMFC.

The complexity of the balance of plant of a fuel cell-fuel processor unit challenges the design and development of compact and user friendly fuel cell power systems for mobile applications. Recent advances in the design and development of materials, such as polymer electrolyte membranes (e.g. ADVENT TPS® high-temperature polymer electrolyte), electrocatalysts and methanol reforming catalysts [1,2] allow the operation of PEMFCs at temperatures at ~200°C. An attractive configuration which would take advantage of the HT-PEMFC features would be the incorporation of fuel reformer inside the fuel cell stack [1,2], either in separate compartments or directly adjoined with the anode electrodes of the stack, so that methanol reforming takes place inside the fuel cell stack (Internal Reforming Methanol Fuel Cell, IRMFC). This requires the development of highly active and selective methanol reforming catalysts, which will be able to operate at temperatures as low as possible with minimal CO formation. Recently, a single-cell of a high-temperature, polymer electrolyte fuel cell incorporating ADVENT TPS® phosphoric acid doped copolymer and a methanol reforming catalyst in the anode has been already constructed and tested at 200°C demonstrating the functionality of the IRMFC unit. Specific targets for improvement of the efficiency have been also identified and recent advances are presented in the present work. These include the activity of the reforming catalyst and the thermal stability of the membrane for operation above 200°C.

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V-11

CONVERSION OF OIL-SLIMES WITH PRODUCTION METHANOL AND FUEL COMPONENTS

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Industrial activity of the oil refining and oil and gas extraction enterprises inevitably renders negative influence on objects of the natural environment. Critical factor for ecology of oil-field regions is floods of a significant amount of oil and oil-based waste products - oilslimes, being sources of environmental contamination. On volumes of total environmental contamination, the oil-and-gas industry costs on the third place, after color and ferrous metallurgy to which she concedes on volumes of emissions on 10-15 %. According to statistics of the oil-extracting companies, losses of oil at her transportation and storage reach 2,5 % from total amount of extraction, and in territory of the Russian Federation than 3 million tons of oilslimes is annually formed more.

The Open Company "*EcoBioCatalis*" brings to attention own technology of oilslimes processing. The technology is realized with application of installations of preliminary electromagnetic oilslimes processing weights with the further them oxidizing gasification in special devices full thermal destruction and with the subsequent catalitic synthesis on the basis of the received gas mix of valuable chemical components - methanol, motor fuels standards of EURO - 4 and EURO - 5, BTX, etc.

The offered technology is intended for oilslimes processing and sour sulfur-containing tars of a wide spectrum of physical and chemical structures.

Advantages of offered technology:

1) An opportunity of reception of production with high market cost: methanol, fuel components standards of EURO - 4 and EURO - 5, BTX, etc.;
2) An opportunity of extraction of sulfur from initial hydrocarbonic raw material in a case oilslimes with the high of sulfur contents, and also in case of use of sour tars;
3) An opportunity of extraction of heavy metals as the cindery rests;
4) External non-volatility of a full work cycle;
5) A continuity and an opportunity of automation of the majority of technological stages;
6) High efficiency on initial oilslimes;
7) Hardware independence of some separate key stages from each other: receptions primary a hydrocarbonic phase, gasification of a hydrocarbonic oilslime phase, synthesis of methanol and synthesis of fuel components;
8) An opportunity of clearing of a residual water phase up to a level of oil impurity, and also the heavy metals corresponding to standards of nature protection zones;
9) The ecological cleanliness expressed in absence of harmful gas, liquid and firm waste products of processing.

ELECTROMAGNETIC REACTOR OF WATER TREATING FROM OILS AND HYDROCARBONS

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The problem of clearing of water resources from oil pollution is rather actual now. Annual total emission of mineral oil in the seas and oceans as a result of consequences of extraction and emergencies is estimated on different sources, including the National academy of sciences the USA on the average from 6 up to 8 million tons. Nevertheless, the problem of operative and effective liquidation of consequences of similar emissions is far from the decision in view of low efficiency of existing technological decisions, and including, absence high-efficiency the reactor equipment. The majority of known processes of clearing of water environments from oil pollution is based on use the methods of oxidation **[1]**, flotation **[2]**, absorbtion **[3]**, and also methods of biological clearing **[4]**. Under the total characteristics, including productivity, a degree of clearing, simplicity of technological decisions, the economic and power efficiency, the mentioned ways are conditionally suitable for the decision of similar problems.

The clearing process of water environments from oil pollution and dangerous hydrocarbons aromatic and olefinic the lines, based on use is developed and tested in industrial scale as basic reactionary unit of the device of electromagnetic processing water environments. The principle of work is based on the phenomenon of acceleration microparticles association of mineral oil in conditions of interaction of an external variable magnetic field with ferromagnetic sorbent which particles have own constant magnetic field. As a result of such interaction there are intensive association processes the hydrocarbonic components being consequence of concentration in places of impacts of ferromagnetic particles of electromagnetic, thermal and mechanical energies. Further, passing through the polysorbtional layers, the integrated particles of hydrocarbons are absorbed much faster, than similar particles of smaller diameter.

Working parameters of a reactor electromagnetic association:

Initial concentration of mineral oil — 100 ÷ 1 mg/L

Final concentration of mineral oil — 0,5 ÷ 0,05 mg/L

Working volume of a reactor — 30 L

Productivity on initial water — Up to 100 m^3/h

Operating mode — Continuous

Working temperature — 0 ÷ 50ºC

Working pressure — 0 ÷ 1,0 MPa

Besides direct use of the specified installation during water treating, there are variants of her modification, allowing her use in a number of adjacent tasks of oil extracting and processing. In particular, her use is planned during preliminary processing, tars, bitumen sand, in manufacture of dyes, etc. spheres.

The general distinctive characteristics of installation:

1) High efficiency

2) Stability to a high level of pollution of communications (a rust, sand, fine stones)

3) Standardization of a design with an opportunity of fast replacement of elements (a grid, a pipe, nozzles and so forth)

4) Absence of a problem of deterioration in case of use the plastic case of a reactor

Installation has passed industrial tests in a zone of the Caspian pool: Russia, Republic Dagestan. On a method of clearing of water environments from mineral oil with participation of the described device the patent of the Russian Federation - №2371232 « THE METHOD OF CLEARING OF THE WATER ENVIRONMENT FROM MINERAL OIL», a priority - from 27.06.2008 is received.

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FAST PYROLYSIS OF BIOMASS IN FLUID BED WITH MICROWAVE HEATING: A PRELIMINARY ANALYSIS WITH CFD MODELING

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The search for sustainability instigates the investigation for alternative sources of energy, in order to mitigate economic, social and environmental problems. Thus, biomass appears as one important renewable source for the production of food, materials, chemicals, fuels and energy, being essential to develop processes and equipment to convert its resources efficiently.

Several biochemical and thermochemical processes have been investigated for biomass processing, but thermochemical methods have been shown as the easiest to adapt to the existing energy infrastructure.

In this context, fast pyrolysis has emerged as a promising alternative, consisting in the conversion of biomass into a complex mixture of organic compounds and fractions of char and gas [1; 2]. The main product of this process is the bio-oil, which can be used in engines and turbines, or fed into refineries to obtain products with higher added value [2].

Fluid beds are the most popular configuration used in fast pyrolysis, due to their ease of operation and ready scale-up, allowing to obtain high yields of bio-oil [3]. At laboratory scale, this reactor is conventionally heated by electric resistances, and at larger scales, by burning by-products of pyrolysis.

Recently, an alternative that is being proposed is the microwave heating, which has been proven to be energy efficient and has been widely accepted as an easy to control technology, resulting in a bio-oil with interesting characteristics for a sustainable manufacturing of chemicals and biofuels, it has also shown favorable energy balances for the process [4; 5; 6; 7; 8; 9; 10; 11].

Aiming to understand and develop this process, the software COMSOL Multiphysics® was used for the simulation of thermal behavior in the fluid bed with microwave heating. The results permit to make a preliminary analysis of the thermal behavior of biomass, the distribution of electric field and resistive losses in the oven, and also its influence on the homogeneity of heating and on the bio-oil yield obtained.

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HYDRODYNAMIC INTERACTION AND BUBBLE COALESCENCE LAWS

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The coalescence of bubbles takes place in many natural and engineering processes. Boiling, flotation, fermentation and oxidation are only a few examples where bubble coalescence plays a primary role. However, by virtue of the complexity of this phenomenon the physical laws of bubble coalescence are not yet well understood. The most widely accepted mathematical models are based on the so-called "drainage mechanism" coalescence. These models contain at least two (or three) adjustable parameters, and they make some assumptions about the conditions of drainage of the liquid film (viscous or inviscid mechanism and others). In addition, the limits of applicability of the drainage mechanism have not yet been experimentally determined. Suffice it to say, “drainage models" cannot explain why bubble coalescence is absent in flows of micro-bubble media [1], but in the ultrasonic field, coalescence of micro-bubbles takes place [2]. In order to explain these experimental facts the author has proposed that the coalescence of bubbles is essentially dependent on the character of the hydrodynamic interaction when they approach each other. Therefore, our investigations of the problem of bubble coalescence were based on the hypothesis, that the result of the collision of bubbles (coalescence or no coalescence) is completely determined by the dimensionless parameters of the liquid and bubbles before the collision. In this case, there is no need for any assumptions about the physical mechanisms (drainage or another) of the process of bubble coalescence. In the general case, the problem of bubble collision and coalescence is described by six dimensional quantities: ρ, μ, σ, $d_i, d_j, U_i, U_j, (d_i < d_j)$. In accordance with the π-theorem of the dimensional theory, these quantities form only four independent dimensionless criteria. We choose two criteria the Reynolds number and the Weber number which was used in the “drainage models» and in the paper [3]: $e = \frac{\rho U_n d_{ij}}{\mu}$, and $We = \frac{\rho U_n^2 d_{ij}}{\sigma}$. Where: $U_n = (U_i - U_j)n$ is the velocity of bubble approach, n is a unit vector directed from larger to smaller bubbles along the line connecting centers of the bubbles, $d_{ij} = {2d_i d_j}/{(d_i + d_j)}$

is the equivalent diameter of the bubbles, ρ, μ and σ are the density, viscosity and surface tension of the liquid, respectively. The third and fourth criteria are the Reynolds and Weber numbers, based on the absolute (rise) velocities [4,]: $R_t = \frac{\rho U_t d_t}{\mu}$, and $W_j = \frac{\rho U_j^2 d_j}{\sigma}$. The author’s experimental data [5] were used together with data available in the literature to develop a dimensionless correlation for predicting the bubble coalescence probability in this way. It was found that at low Weber numbers $We < 1$ the dependence of bubble coalescence on the Weber number (from 10^{-8} to 1) is degenerated and there is only dependence on the Reynolds number, which we call the law of the critical Reynolds number. This law limits the coalescence of the bubbles from below, from the low Reynolds numbers (or small size of the bubbles). At Reynolds numbers $Re < Re_c \approx 30$ the coalescence of bubbles in the liquid is absent. The second law of coalescence, at Reynolds numbers $100 < R_t < 100$, which was substantiated by Duineveld’s experiments [4] we call the law of the critical Weber number restricts the bubble coalescence from the top (from the large bubbles). In this case the dependence of bubble coalescence on the third dimensionless criterion R_t degenerates and there is only dependence on W_j. At Weber numbers $W_j > W_c \approx 5$ the coalescence of bubbles in the liquid is absent. The condition of bubble coalescence for the new dynamic model based on these coalescence laws can be presented as $P_{tj} = \left\{\begin{matrix} 1, & if\ Re > Re_c\ and\ W_j < W_c \\ 0, & if\ Re < Re_c\ or\ W_j > W_c \end{matrix}\right\}$, where P_{tj} is the coalescence efficiency (or probability) of bubbles. Validity of the basic models of bubble coalescence including a dynamic model was investigated. It was shown that the proposed dynamic model of bubble coalescence gives the best description of the coalescence process.

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THE MECHANISM OF CARBON MONOOXIDE LOW-TEMPERATURE OXIDATION BY MOLECULAR OXYGEN OVER $PdCl_2$-$CuCl_2$/γ-Al_2O_3 CATALYST

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The reaction of carbon monooxide low-temperature (15-100°C) oxidation by oxygen is of fundamental scientific interest, because it is one of the simplest oxidation reactions and can be used for the development and verification of general laws governing the oxidation processes.

Among low-temperature catalysts of this test reaction, supported metal complex catalysts are least studied. In this group, catalysts combining on the palladium and copper active sites are very promising [1-3]. This report deals with new data about the state of active components on the surface of the $PdCl_2$-$CuCl_2$/γ-Al_2O_3 catalyst and the mechanism of the low-temperature oxidation of carbon monooxide.

The structure of freshly prepared $PdCl_2$-$CuCl_2$/γ-Al_2O_3 catalyst was studied by X-ray absorption spectroscopy (XAS), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) [4]. All measurments were conducted at room temperature. It was shown that copper and palladium occur on the surface of γ-Al_2O_3 in the forms of crystalline of $Cu_2Cl(OH)_3$ (paratacamite) and chemisorbed mononuclear $PdCl_4^{2-}$ anions, respectively. According to XAS data, the local environment of palladium consist of four chlorine atoms in a square planar coordination with one slightly elongated an Pd-Cl bond. The evolution of the local environent of copper and palladium upon transition from the initial salts to the impregnation solutions and active species on the surface of γ-Al_2O_3 was tracked. No evidence of close contacts between copper and palladium within the active sites in the freshly prepared catalyst was found.

DRIFTS spectra measured *in situ* indicate that both linear (2114 cm^{-1}) and bridging (1990 and 1928 cm^{-1}) coordinated carbon monooxide emerge upon CO adsorption on the catalyst’s surface. Furthemore, the formation of CO_2 upon the interaction of coordinated CO with atmospheric oxygen was detected. This implie the direct involvement of oxygen and water in the formation of CO_2 from CO.

No significant change in the effective chemical state of Pd and Cu atoms (as monitored by *in situ* XAS) is detected in the presence of dry carbon monooxide stream (0.01% CO + N_2). On the other hand, prolonged exposure of the catalyst to similar atmosphere with traces of humidity (0.01% CO + N_2 + H_2O) led to partial reduction of Cu(II) to Cu(I) and Pd(II) to Pd(0). Meanwhile no significant change in the active components state was again detected in the oxidative reaction atmosphere (0.01% CO + 2.00% O_2 + N_2 + H_2O). The latter fact can be rationalized assuming that modified be active forms of the catalyst are present under the reaction conditions only in minor quantities.

The kinetic regularities were studied at 18-40°C and atmospheric pressure of CO, O_2, N_2, H_2O(gas) mixture in a flow reactor (steady state conditions). The activation energy reaction is found to be negative (-40 kJ/mole*K). The empirically derived equation for the rate of carbon dioxide formation is as follows (1).

$$r_{CO_2} = kP_{CO}^{0.2}P_{H_2O}^{1.7}P_{O_2}^{0.8} \tag{1}$$

The high kinetic orders for water and oxygen partial pressures allowed us to propose mechanisms with the participation of both (O_2 and H_2O) reagents in steps of carbon dioxide formation.

Alternative mechanisms of this reaction are discussed.

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BUILDING OF ALKYLATION PROCESS MATHEMATICAL MODEL TAKING CHANGES OF LIQUID CATALYST ACTIVITY INTO ACCOUNT

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An important stage in production of synthetic detergents is the stage of benzene alkylation with higher olefins C_{10}-C_{14} to obtain linear alkyl benzene (LAB) [1].

It is obvious that problem of LAB production increasing is relevant at domestic plants, because the need for it is growing both in the domestic market and abroad. Mathematical modeling in this case is an indispensable tool for studying the influence of various parameters on the process and allows to choose optimal technological parameters in order to increase the yield of product with desired quality.

For development of an adequate mathematical model of alkylation process it was necessary to investigate it and describe mathematically and, finally, to take changes in the activity of catalyst during implementation of this process in chemical reactor into account.

The first stage of this work was to identify factors influencing the activity of catalyst - hydrofluoric acid, the second – supplement of existing reactor mathematical model [2] with drawn up functions of HF deactivation.

Mathematical model of the alkylation process was supplemented by developed functions describing:

- Change in the concentration of catalyst in dependence on concentration of unsaturated disubstituted aromatic compounds;
- Changes of main chemical reactions rates in dependence on concentration of pure catalyst;
- Changes in the concentrations of unsaturated aromatic compounds in dependence on HF concentration.

For example, the function describing the rate of benzene with olefins alkylation in dependence on concentration of pure catalyst can be written as following [3]:

$$W_1 = k_1 \cdot C_{ol} \cdot C_{benz} \cdot e^{a \cdot C_{HF}} ,$$

where W_1 – rate of chemical reaction, mole/m^3·sec; k_1 – reaction rate constant, m^3/mole·sec; C_{ol}, C_{benz}, C_{HF} – concentrations of olefins, benzene and pure HF relatively, mole/m^3; a – coefficient, depending on catalyst and reaction type.

With help of benzene alkylation process mathematical model optimal ranges of some technological parameters were identified:

- Molar ratio of benzene olefins: 6-8, depending on raw materials composition;
- Weight ratio of HF/LAB: not less than 1.2 for T = 55 ° C;
- Weight ratio olefins/diolefins: about 85;
- Temperature: 50 to 55 °C, depending on raw materials composition.

Thus, complementation of created earlier mathematical description with functional dependencies taking changes of catalyst activity into account allowed to increase the adequacy and predictive ability of model.

Thus, this model can predict changes in HF catalyst activity in dependence on concentration of unsaturated aromatic compounds that increases the accuracy of output parameters calculation (LAB bromine index and heavy alkylate bromine number), and therefore to optimize the process of linear alkyl benzene production. Operation of industrial alkylation reactor, while maintaining the optimum technical parameters will allow to receive not less than 7.5 tons/day of LAB of high enough quality.

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TRI-REFORMING AND PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS OVER POROUS NICKEL BASED CATALYSTS

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In recent years the catalytic processes of the tri-reforming of methane (TRM)– mixed CO_2-H_2O-O_2-reforming and the partial oxidation of methane (POM) to synthesis gas have been developed. They give the possibility to use renewable energy sources, for example, biogas for generation of synthesis gas. The major problems encountered towards the application of these processes are local overheatings, sintering and oxidation of the active component in the inlet part of the catalyst bed in the presence of oxygen in the gas phase and the carbonization of the catalyst in the catalyst bed region, where steam and carbon dioxide reforming of methane occurs. To enhance heat transfer efficiency of the catalyst it is reasonable to use high thermal conductive metallic support of catalyst. The aim of this work was to study the catalytic properties of the nickel catalysts supported on metallic ribbon porous nickel with the MgO underlayer in TRM and to test the developed monolithic catalyst in constructed pilot reactor of POM.

The catalysts contained 1.5-2.0 wt. % Ni and 5.0 wt. % MgO, supported on the 0.1mm thick ribbon porous nickel, obtained by rolling (S_{sp} - 0.15 m^2/g, V_{Σ} - 0.1 cm^3/g). The catalysts were characterized by XRD, low-temperature adsorption of nitrogen, SEM and TEM in combination with EDX analysis. Catalytic activity in TRM to synthesis gas was estimated by the flow method (1atm., 750°C, CH_4-23.0 vol. %, CO_2-5.7 vol. %, H_2O-5.4 vol. %, 65.9 vol. % air, feed rate of the reaction mixture -25.0 l/h, m_{cat} = 0.40g). Prior to testing the catalysts were reduced at 750 - 900°C in H_2 flow.

According to the TEM data the supported nickel crystallites are highly dispersed (2-5 nm) and epitaxially bound with the MgO surface. Figure 1 shows the effect of time-on-stream in the TRM (9 h) on CH_4 conversion. During the testing the methane conversion decreased by no more than 4-9 rel. %. The most stable activity was observed for the sample reduced at 900°C. The oxygen conversion was 98-99 % and did not decrease with the reaction time. TEM data indicate that after testing in the samples a part of supported nickel crystallites retains its stable state as dispersed crystallites of metallic nickel (3-10 nm) epitaxially bound with MgO; no carbon is detected in the catalysts after testing.

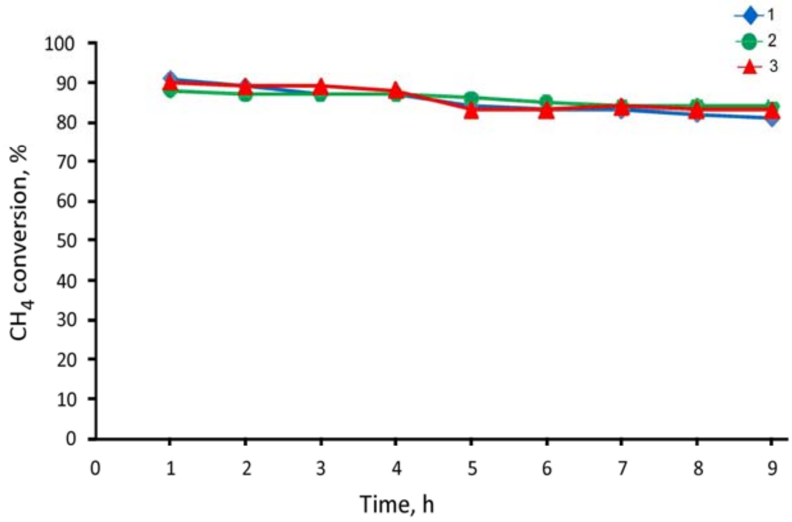

Fig.1. CH_4 conversion versus time-on-stream in the TRM over catalysts : 1 -1.5 % Ni/ rpNi + 5.0 % MgO, 750°C, H_2; 2 -1.5 % Ni/rpNi + 5.0 % MgO, 900°C, H_2; 3 -2.0 % Ni/rpNi + 5.0 % MgO, 750°C, H_2.

The supported nickel catalyst 3.0 % Ni/rpNi + 5.0 % MgO was used to prepare a cylindrical axial monolith consisting of alternating flat and corrugated ribbons (corrugation height 2mm, monolith diameter 36 mm and height 54 mm, catalyst volume in the monolith 5.0 cm^3).Testing was performed under an autothermal regime, the reaction zone was preheated to 500 °C, the feed mixture contained 23 vol. % of natural gas in air. Table lists the test data for the monolith catalyst in partial oxidation of natural gas carried out in a flow reactor.

Table. Parameters of partial catalytic oxidation of natural gas.

Flow rate, L/min		τ, s	T cat., °C		CH_4 conversion, %		Selectivity, %		$CO + H_2$, vol.%	
Natural gas	Air		Inlet	Outlet	Experi-mental	Equili-brium	for CO	for H_2	Experi-mental	Equili-brium
5.0	16.3	0.15	829	732	97	97.04	88	97	47	50.44
8.4	27.7	0.09	921	797	98	99.33	88	88	47	51.86
16.8	58.8	0.04	1023	941	90	99.97	82	82	41	52.41

At the contact time 0.09-0.15 s experimental values of methane conversion and synthesis gas yield are close to the calculated equilibrium values. TEM results showed that no carbon deposition was in catalysts (after 9 hours on stream).

Thus, the developed nickel catalysts supported on the ribbon porous nickel with MgO underlayer are active and stable in TRM and POM to synthesis gas.

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OPTIMIZATION OF HARDWARE DESIGN OF PARAFFINS DEHYDROGENATION PROCESS USING MATHEMATICAL MODEL

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One of the main problems arising in the operation of existing industrial units of refining and petrochemical facilities operating under high pressures and temperatures, is to ensure the optimum conditions in terms of energy and resource efficiency. This problems should be solved with taking conjugacy of thermal and reaction processes into account, as well as mutual influence of modes of heat transfer and reactor equipment. At the present time to solve such problems mathematical modeling techniques are successfully applied [1,2].

In this scientific research discussed optimization of hardware design on example of higher alkanes dehydrogenation process is discussed.

The equations of material and heat balance for plug flow reactor were built [3]:

$$\frac{\partial C_i}{\partial t} = -u\frac{\partial C_i}{\partial l} \pm W_j$$

$$\rho^m C_3^m \frac{\partial T}{\partial t} = -u\rho^m C_3^m \frac{\partial T}{\partial l} \pm \sum_{j=1}^{n}(-\Delta H_j)W_j$$

Her ρ^m – mixture density, kg/m^3; $C_p{}^m$ – mixture heat capacity, J /(mole·K); T – temperature, K; ΔH_j – heat effect of reaction; u – flow linear velocity, m/sec; c_i – concentration of substance, l/mole; l – reactor length; t – time; W_j – reaction rate.

Mathematical models of heat exchanger and furnaces, which are heat-balance equations, were also developed.

Computer modeling system «LAB-LABS» based on time-dependent kinetic model paraffins dehydrogenation process on the basis of formalized mechanism of hydrocarbons on Pt-catalysts conversion was developed.

Using a block of module, describing various units of technological scheme revealed the following main ways of process optimization:

1. The establishment of mutual influence of processes and devices allows the development of models that provide versatility and value of the mathematical description for a wide variation of process conditions.

2. Reconstruction of existing single pass heat exchangers will reduce electricity consumption by 3400 kW • h in the raw materiails in the furnace heating stage. This corresponds to more than 2.5 tons of fuel oil per year. Replacing the shell and tube heat exchanger by the plate one will provide energy-efficient modes of heating equipment and reduce energy consumption at 7800 kW • hr or 5.7 tons of fuel oil per year.
3. Improving of higher alkanes process dehydrogenation efficiency is achieved by providing additional recycling of unreacted paraffins, which can increase the depth of processing of raw materials to the level of 45-46%. The optimal ratio of recycled wax depends on the composition of raw materials and the degree of deactivation of the dehydrogenation catalyst and can be 0.1-0.7.
4. Reconstruction of existing heat transfer equipment, providing raw material to the heating temperature 390 °C, improves the efficiency of production by reducing of energy consumption of raw materials in the furnace heating stage (26.7%).
5. Transition to double-reactor scheme will increase the productivity of industrial plant by an average of 71%. For CD-3 catalyst in the reconstruction of heat exchanger and an increase in consumption of raw materials up to 120 m^3/h conversion yield is increased by 82 tonnes/day. Replacing of heat exchanger by the plate one and increasing of raw materials consumption up to 150 m^3/h conversion yield is increased by 126 tonnes/days. Provision of heating equipment is limited to consumption of raw materials 150 m^3/h.

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DEVELOPMENT OF KINETIC MODEL FOR BENZENE WITH ETHYLENE ALKYLATION PROCESS

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Alkylation of benzene with ethylene is the main direction of benzene consumption (50% of total amount) [1]. Obtained ethylbenzene is an intermediate for organic synthesis, especially in production of styrene and synthetic rubber. It is used as a solvent or diluent, a component of automotive and aviation fuels, as well as in production of cellulose acetate. Therefore, improving resource efficiency of this process is an urgent task.

Methods of mathematical modeling and developed on its basis computer modeling systems are an effective tool for selecting of industrial plants work directions improvement, avoiding considerable material and time costs in the production of natural experiment, limiting by computing one.

After the analysis of flow composition and existing ideas about chemism of benzene with ethylene alkylation process [2] the list of reactions in the alkylation reactor was drawn up (Table 1). The thermodynamic possibility of their occurrence was confirmed by calculation of isobaric-isothermal parameter - the Gibbs energy change ΔG.

Table 1. ΔG values for reactions (T = 395 K, P = 0.15 MPa)

№	Reaction	ΔG, kJ/mole
1	Benzene + Ethylene= Ethylbenzene	-47,9
2	Ethylbenzene + Ethylene = Diethelbenzene	-61,4
3	Diethylbenzene + Ethylene =Triethelbenzene	-32,2
4	Benzene + Diethylbenzene =2Ethelbenzene	-13,6
5	Benzene + Triethelbenzene =Diethylbenzene+ Ethylbenzene	-15,7
6	Ethylene + Ethylene =Butylene	-73,8
7	Benzene + Butylene =SBB	-11,3
8	Benzene +Propylene =IPB	-28,3
9	Toluene + Ethylene =Ethyltoluene	-54,6
10	2 Benzene + Ethylene =DPA	-0,4
11	6 Benzene =Coke+12 Hydrogen	-1305,1
12	2 Benzene + Ethylene =2Toluene	-138,0
13	Ethylene + Hydrogen=Paraffin	-17,6

Here SBB - secondary butylbenzene, IPB - isopropylbenzene, DPA – diphenyletan.

Expressions for rates of reactions occurring in benzene with ethylene alkylation process are shown in Table 2.

Reaction type	Expression for rate of reaction
Alkylation	$W_1 = k_1 \cdot C_{\text{Benzene}} \cdot C_{\text{Ethylene}}$
Transalkylation	$W_4 = k_4 \cdot C_{\text{Benzene}} \cdot C_{\text{Diethylbenzene}}$ $W_5 = k_5 \cdot C_{\text{Benzene}} \cdot C_{\text{Triethylbenzene}}$
Coke formation	$W_3 = k_3 \cdot C_{\text{Diethylbenzene}} \cdot C_{\text{Ethylene}}$ $W_{10} = k_{10} \cdot C^2_{\text{Benzene}} \cdot C_{\text{Ethylene}}$ $W_{11} = k_{11} \cdot C_{\text{Benzene}}$
Diethylbenzene formation	$W_2 = k_2 \cdot C_{\text{Ethylbenzene}} \cdot C_{\text{Ethylene}}$
Butylene formation	$W_6 = k_6 \cdot C^2_{\text{Ethylene}}$
SBB formation	$W_7 = k_7 \cdot C_{\text{Benzene}} \cdot C_{\text{Butylene}}$
IPB formation	$W_8 = k_8 \cdot C_{\text{Benzene}} \cdot C_{\text{Propylene}}$
Ethyltoluene formation	$W_9 = k_9 \cdot C_{\text{Toluene}} \cdot C_{\text{Ethylene}}$
Toluene formation	$W_{12} = k_{12} \cdot C^2_{\text{Benzene}} \cdot C_{\text{Ethylene}}$
Paraffin formation	$W_{13} = k_{13} \cdot C_{\text{Ethylene}} \cdot C_{\text{Hydrohen}}$

Then kinetic model of the process can be written as follows:

$$\begin{cases} \dfrac{dC_{Benzene}}{dt} = -W_1 - W_4 - W_5 - W_7 - W_8 - 2W_{10} - 6W_{11} - 2W_{12} \\ \dfrac{dC_{Ethylene}}{dt} = -W_1 - W_2 - W_3 - 2W_6 - W_9 - W_{10} - W_{12} - W_{13} \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ \end{cases}$$

Initial conditions $t = 0$, $C_i = C_{0i}$, where i – corresponding hydrocarbon.

The further stage of research will be mathematical description of alkylation process, its software implementation and optimization of technological mode.

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BEHAVIOUR OF OLIVINE AND γ-ALUMINA AS PRIMARY CATALYST IN STEAM GASIFICATION OF PINEWOOD SAWDUST IN A CONICAL SPOUTED BED REACTOR

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Biomass is considered to be one of the most promising alternatives to fossil fuels and feedstocks. One of the technologies that has good perspectives for industrial development is gasification in order to obtain a valuable gas than can be used as synthesis gas or to produce hydrogen. Hydrogen represents a clean alternative to fossil fuels provided that it can be produced from renewable sources. Steam has been used as gasification agent because the main objective is to maximize hydrogen yield. The utilization of steam as the unique gasifying agent requires an external heat supply due to the endothermic nature of the steam gasification reactions [1].

A conical spouted bed reactor (CSBR) has been used in this study. This reactor is suitable for the handling of particles of irregular texture, fine particles, sticky solids and those with a wide size distribution, due to its great versatility [2, 3].

The behavior of olivine and γ-alumina as primary catalysts (tar removal catalysts) over the gasification process has been studied. The olivine was calcined at 900 °C before de reaction. The gasification temperature was 900 °C and biomass to water ratio was maintained at 1:1 in all runs. Product distribution has been monitored on-line by means of a thermostated line, using a HP 6890 gas chromatograph to quantify tar and a Varian 4900 micro-gas chromatograph for gaseous products. Product identification has been carried out by means of a mass spectrometer (Shimadzu QP2010S).

The products obtained in the gasification have been classified into three different fractions: gas, tar (containing benzene and compounds of higher molecular weight) and char. The main effect of olivine and γ-alumina is the increase of the gas fraction due to the cracking of tars. In the presence of olivine and γ-alumina the fraction has been reduced from 15 % (operating with a bed of sand) to 6% and 4% respectively, moreover, a significant increase of the gas production from 76.7 % to 86% and 87.6% has also been obtained.

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The combined use of a catalyst and steam resulted in an increase of H_2 and CO_2 and a decrease in the CH_4, CO and C_nH_m contents (see Fig. 1). Thus, the use of primary catalyst provokes an improvement of the H_2/CO ratio of the syn-gas produced [4]. These trends are caused by both the cracking of the tars and the greater importance of the water-gas shift and reforming reactions.

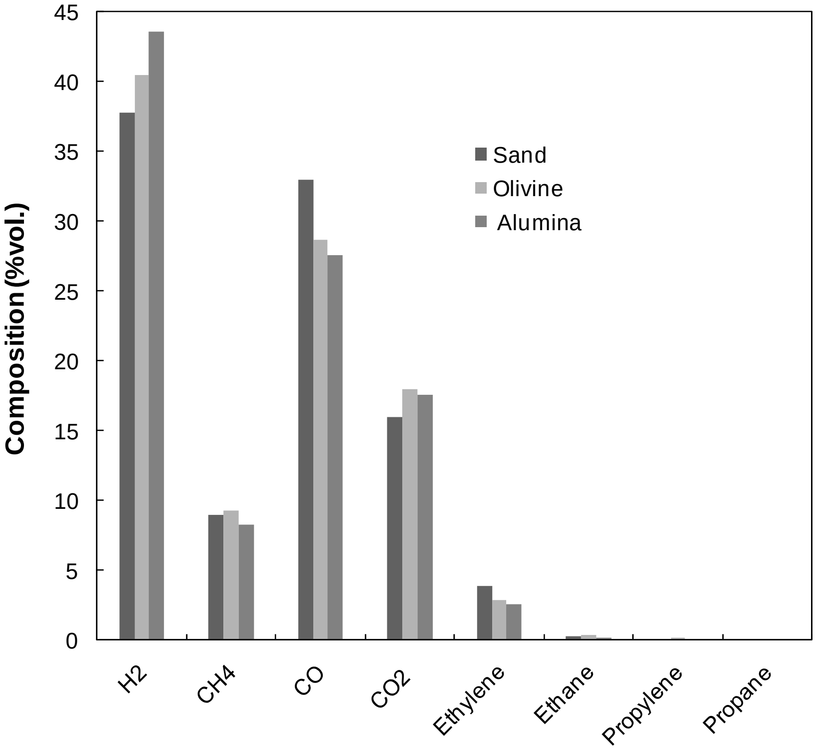

Figure 1. Influence of olivine and γ-alumina in the composition of gaseous product.

The tar fraction has been characterized and the compounds have been divided into four different groups: heterocyclic, aromatics, light polyaromatics and heavy polyaromatics. Using olivine or γ-alumina in the gasifier, the tar fraction is mainly composed of light aromatics (57 and 61 %), however operating with sand beds the prevailing compounds of the tar are heavier, as observed by other authors [5].

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SYNTHESIS OF ZSM-5 BY FACTORIAL DESIGN AND ACTIVITY FOR CATALYTIC FAST PYROLYSIS OF BIOMASS

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Catalytic fast pyrolysis (CFP) is a thermochemical process in which biomass is directly converted into liquid fuels and basic chemicals. This process involves a fast heating of biomass under inert atmosphere at up to 700°C in the presence of a catalyst. For cellulosic materials, this process causes the rupture of highly oxigenated coumpounds, producing furans as intermediate products [1,2]. These intermediates can be processed in the presence of a catalyst, producing aromatics and olefins through a series of decarbonylation, decarboxylation, dehydration, and oligomerization reactions [3,4]. In this work, samples of ZSM-5 catalyst were synthesized according to a design of experiments and their activity for fast pyrolysis was evaluated using Thetrahydrofuran as a model compound.

Experimental: The catalysts were synthesized as described by Ghiaci et al [5], using a design of experiments varying the temperature and time of synthesis. The characterization of the catalysts samples was done by surface area measurements, X-ray diffraction (XRD) and ammonia temperature programmed desorption (NH3- TPD). CFP experiments were performed in a fixed bed reactor at 500°C. The reagent was injected into a nitrogen stream by a syringe pump. The space velocity was kept constant at 2.5 h^{-1}. The products were analyzed by on-line gas chromatography using FID and TCD detectors. The spent catalyst was characterized by TPO analysis to obtain carbon amount.

Results: The results indicate the existence of an optimal time of synthesis to obtain a ZSM-5 with crystallinity and acidity suitable for the fast pyrolysis reaction. The X-ray diffraction patterns for synthesized ZSM-5 are shown in Figure 1a. It is possible to observe that the samples presented diffraction patterns characteristic of ZSM-5 and the increase in time of synthesis favored the crystallinity of the material. The NH_3- TPD curves for the catalysts are shown in Figure 2b. It can be seen that there are two peaks centered at ~250°C and ~470°C. The increase in the time of synthesis increased the intensity of peaks and, consequently, the acidity of the sample.

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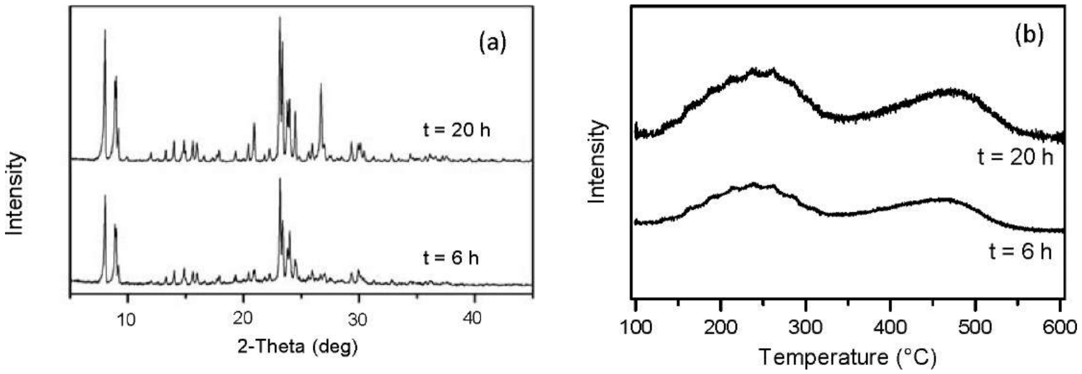

Figure 1. (a) X-ray diffraction patterns and (b) temperature programmed desorption of ammonia for synthesized catalysts.

Figure 2 shows the results for CFP reaction obtained using samples of the synthesized catalyst. A commercial sample of ZSM-5 was also evaluated in order to provide reference. The synthesized catalysts presented good conversion of thetrahydrofuran, although their selectivity for heavy compounds, like benzene and toluene, was smaller than the one obtained with commercial ZSM-5.

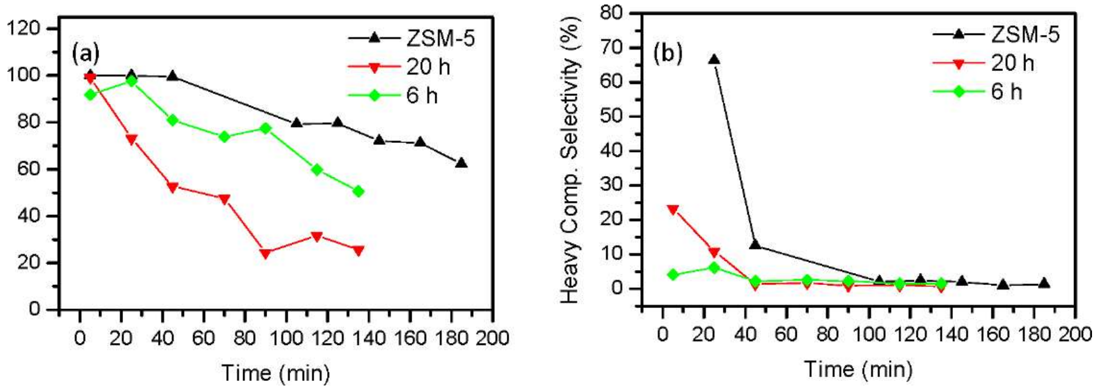

Figure 2. (a) Conversion and (b) selectivity for synthesized catalysts.

Due to the lack of space, results for the temperature of synthesis and evaluation of its influence on the catalysts properties and activity were not shown. In a subsequent step, an additional time of synthesis will be added for a better evaluation of its influence. All catalysts will have their activity for CFP evaluated.

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EXTERNAL MASS AND HEAT TRANSFER IN MULTIPHASE EXOTHERMIC REACTIONS – OSCILLATORY MOTION OF THE LIQUID PHASE IN THE PORE SYSTEM OF A CATALYST

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In the field of heterogeneous three-phase catalytic reactions, the knowledge of heat and mass transfer around and inside a catalyst pellet plays an important role. The relevance to the prediction of process behaviour, to the scale-up or the scale-down as well as to design aspects is obvious, especially, with respect to economic efficiency and safety. Conventional approaches to develop mass and heat transfer correlations only consider the hydrodynamic properties of a reactive system. Thus mass and heat transport phenomena are described only by using dimensionless numbers like Reynolds, Prandtl or Schmidt. No particular attention is paid to a possible influence of chemical reactions. Our studies shed light on a fundamental understanding of external mass and heat transfer in catalysed gas-liquid/liquid reactions. The influence of a chemical reaction, namely the formation of gas and/or vapour bubbles by the means of heat generation are investigated. Discrepancies from the classical description of transport phenomena are pointed out theoretically and are verified by experimental results for certain conditions.

Oscillations in three-phase exothermic reactions

In case of exothermic reactions, the periodical formation of (gas-vapour) bubbles can occur, if heat release reaches a certain critical value. Such behaviour can be explained by the following mechanism.

While heating up the liquid inside a catalyst's pore, the partial pressure of vapour increases. As soon as the total pressure of vapour and of saturated gas exceeds a maximum possible pressure inside the pore, the bubble comes into being. The growing bubble displaces the liquid until the pore is empty and the reaction ceases and the generated heat dissipates. Due to high capillary forces the empty pore is refilled nearly instantaneously and bubble formation restarts again.

Owing to this oscillatory motion, there is a significant change in the hydrodynamic and the diffusional behaviour around the catalyst particle and in the catalyst bulk. Based on these considerations, conventional correlations to describe mass and heat transfer are not suitable.

Experimental setup and investigations

The catalytic hydrogenation of olefines was chosen as a model reaction. In respect to investigations of the phenomena described above, a suitable experimental setup needs to meet some requirements. First, the flow conditions of the liquid around a single catalyst particle with well-defined geometry must be well known and adjustable in a certain range in order to quantify the influence of different flow regimes (Re). The application of an annular gap reactor offers this property if the liquid phase is pre-saturated with hydrogen. Such a system has the great benefit of comparability with more simple two-phase systems (liquid-solid). Second, the temperature inside the catalyst pellet, as well as the temperature of the surrounding liquid phase, has to be detected in order to determine the heat transfer.

Experimental outcomes obtained from hydrogenation of 1-hexene to n-hexane on a single nickel catalyst pellet (6x6 mm) show that external mass and heat transfer depends not only on the hydrodynamics, as stated so far, but also on effects caused by chemical reactions. The impact of the reaction can considerably outweigh the hydrodynamic influence.

Measurements with an inert non-porous system showed that the correlations for heat transfer are true. The inert system composes of a copper pellet with similar geometry to the catalyst pellet, an additional heating inside and the possibility of detection of the surface temperature. The usage of this inert copper pellet offers the opportunity to understand the catalytic system more precisely. The comparison of the results obtained underlines the idea of bubble formation.

In this course, the mechanism and concepts for mass and heat transfer correlations are discussed.

OXYGEN ACTIVATION AND OWGS REACTION OVER Au/CuO-CeO$_2$ BIMETALLIC CATALYSTS

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Introduction

Water-Gas-Shift Shift (WGS) reaction is a key reaction in the purification of hydrogen from hydrocarbons while further removal of CO for hydrogen use in PEM fuel cells is carried out in CO-PROX stage. Catalytic converter in which both WGS and CO-PROX reactions are coupled in a single stage is known as OWGS (Oxygen-enhanced Water Gas Shift), decreasing the total volume of the Fuel Processor Unit, which will be helpful for automotive applications. Several studies have reported that the addition of a small amount of O_2 to the reformed fuel is effective in promoting CO removal by WGS reaction at low temperatures [1]. The objective of this work is to study the activity of CuO/CeO$_2$ and Au-CuO/CeO$_2$ catalysts in OWGS reaction and explicate the promotional effect of gold. In order to elucidate the reaction mechanisms which involve mobility step of O reactive species the $^{16}O_2/^{18}O_2$ isotopic exchange reaction has been studied.

Experimental

Bimetallic Au-CuO/CeO$_2$ catalysts were prepared in two steps: first, 7 wt.% Cu was deposited by IWI on commercial ceria (S_{BET} 227 m^2/g) and calcined at 550 °C; then, 1 wt.% of Au was deposited on the former subtracts by DP. The crystalline structures were analyzed by XRD and redox properties were investigated by H_2-TPR. $^{18}O_2$ isotopic exchange was carried out in order to examine the oxygen surface mobility. Isotopic exchange experiments were carried out in a recycled reactor coupled to a mass spectrometer, with the following in situ pretreatment proceeding: oxidation ($^{16}O_2$) at 500 °C for 1 h → outgassing for 30 min → cooled to room temperature: isotopic exchange starts with the introduction of 65 mbar of pure $^{18}O_2$ into the reactor. Then, temperature is increased from 350 to 550 °C at 2 °C/min. Partial pressures of the oxygen isotopomers P_{32} ($^{16}O_2$), P_{34} ($^{16}O^{18}O_2$), and P_{36} ($^{18}O_2$) were sampled every 10 s. The catalyst activity runs in OWGS reaction were carried out in plug flow reactor at atmospheric pressure (GHSV= 12,000 h^{-1} and WSV= 1.83 NL min^{-1}g^{-1}). The composition of feed gas (in vol.%) was $CO/O_2/H_2O/H_2/CO_2$ =4/0.56/9.4/37.9/3 balanced to He. Also WGS reaction was checked removing oxygen from the feed.

Results and Discussion

Some of the textural and morphological properties of the samples are listed in Table 1. XRD patterns of CuO/CeO$_2$ and Au-CuO/CeO$_2$ do not show diffraction peak of gold and copper species, suggesting that both copper and gold are highly dispersed. TPR profiles of the samples (not shown) for CuO/CeO$_2$ show two reduction peaks below at 100 °C, related to highly disperse copper oxide. The peak at higher temperature centered around 210 °C corresponds to copper species in intimate contact with the support and bigger copper oxide clusters; The reduction profile of Au-CuO/CeO$_2$ sample, show at least two reduction peaks: the absence of clear, separated peak of gold reduction suggests the simultaneous reduction of both highly dispersed copper species and gold (which corresponds to the low temperature peak).

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The calculation of the reaction rate for the isotopic exchange and equilibration experiments was carried out based on the initial-rate method [2] .The temperature at the maximum rate of exchange (T_{max}) is 399 and 413 °C for CuO/CeO_2 and $Au\text{-}CuO/CeO_2$ samples, respectively (Figure 1). Clearly, addition of gold decreases the T_{max}. The total number of oxygen atoms exchanged at 550 °C are 32 and 41 atom nm^{-2} for CuO/CeO_2 and $Au\text{-}CuO/CeO_2$ respectively); in fact, for Co_3O_4/CeO_2, surface oxygen atoms are already totally exchanged by 468 °C, and at 473 °C for $Au\text{-}CuO/CeO_2$.

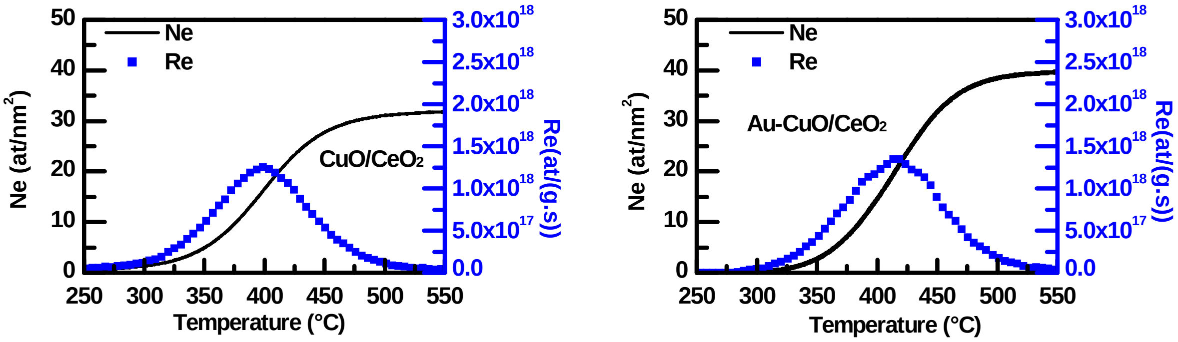

Figure 1. Evolution of the rate of oxygen exchange (Re) and number of oxygen atoms exchanged (Ne).

Both catalysts show very low activity in WGS reaction below 210 °C, as shown in Figure 2. CO conversion in WGS increased with increasing temperature although these catalysts do not achieved the equilibrium under the experimental temperature range. Both catalysts show higher activity in OWGS than in WGS. At around 210 °C the conversion gap of OWGS over WGS was maximized for both catalysts, which exhibit 2 and 4 % of CO conversion in WGS for CuO/CeO_2 and $Au\text{-}CuO/CeO_2$ respectively. Oxygen addition at the feed stream (OWGS) increases the CO conversion to 35 and 40% for CuO/CeO_2 and $Au\text{-}CuO/CeO_2$ respectively. For both catalysts the CO conversion monotonically increases with temperature with the addition of O_2. At 350 °C, WGS became fast enough so that the effect of O_2 addition became less apparent. The activity in OWGS is greatly enhanced by the addition of gold.

Table 1. Textural properties of catalysts.

Catalyst	S_{BET} [a] (m^2/g)	d_p [a] (nm)	d_{CeO2} [b] (nm)
CeO_2	226.0	4.0	7.4
CuO/CeO_2	125.0	4.7	6.2
$Au\text{-}CuO/CeO_2$	115.0	4.9	6.0

[a] Determined by N_2 adsorption-desorption isotherms,
[b] Calculed from X-ray broadening, using Scherrer equation

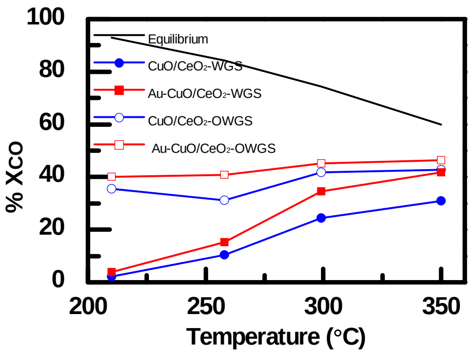

Figure 2. CO conversion vs. temperature in WGS and OWGS reactions

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CHEMICAL AND TECHNOLOGICAL FEATURES OF DRILLING MUD SLIME UTILIZATION

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The modern stage of intense hydrocarbon raw extraction not only entails developments in extraction technologies but also is conjugated with the necessity of solving the problem of drilling waste utilization for oil and gas boreholes.

Water-based and oil-based drilling fluids are used for drilling. Drilling mud wastes are multicomponent and multiphase systems. Utilization direction selection and the design of environmentally pure and profitable technologies for drilling mud waste processing are topical world-scale problems.

This work presents the results of our study of the physicochemical properties of carbonate oil slime, namely, oil based mud cuttings (OBMC), and a technology of its processing is offered.

The composition of OBMC was analyzed. The contents of water, mechanical impurities, hydrocarbons, sulfur, surfactants, pH, density, ash content, chemical oxygen demand, and flash point of the slime were determined. It has turned out to be a three-phase system whose separation requires a technology with the usage of chemical reagents, surfactants.

The elementary composition of the solid residue of drilling slime was evaluated, including calcium, barium, silicon, iron, sulfur, potassium, which were present as minerals: calcite, halite, barite, dolomite, anhydrite, quartz.

The process of thermal slime conversion was explored. Weight loss started from 60°C and was accompanied by a significant endothermic effect with a 140°C DTA maximum. The liquid phase was removed by 240°C. The weight loss was 61–62 wt. %.

Very weak effects related to oxidation of small amounts of organic substances were observed on the DTA curve within 300–360°C. Above 400°C, slow weight loss occurred due to thermal decomposition of the carbonate constituents. The water content in the residue after the thermal treatment according to the technology of Karachaganak Petroleum Operating B.V. (Kazakhstan) was 11 wt. %.

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The technological process of OBMC treatment features after-annealing of the mineral solid residue on a rotating furnace device. The technological process is based on the principle of oil product desorption from the treated material without flame with subsequent burning of the sublimation vapors in an after-annealing chamber. A barrel chamber-breaker is the chief apparatus of the device, through which a spindle with a row of hammer strikers goes. The shaft is motor-operated with the motor powered from a Diesel generator. When the shaft is rotating, the hammer strikers crush solid particles in the wastes, and heat is generated due to friction. Then the wastes are heated above the evaporation temperature of the oil base (260–300°C). The liquid in the wastes is evaporated and leaves the chamber as vapors in few seconds. Then, the vapors of hydrocarbons and water condense in separate condensers. When temperature increases, continuous feed of the hydrocarbon-containing wastes proceeds, and the dried solid residue is removed from the device. To adjust temperature, air and technical water can be fed to the furnace. The temperature of the released gases varies from 370 to 650°C while that of the material is 30–50°C lower. A dust-removal chamber and few cyclones serve for purification of the gases released from the rotating furnace from fly dust.

The surface characteristics of the solid residue after the thermal treatment of OBMC were studied. It possesses a low specific surface (2 m^2/g), since the micropore fraction is very low with macropores to predominate in the bulk. The particle size of the resulted mineral product is distributed within 5–100 µm and more.

A mineral-bitumen composition material on the basis of the solid slime residue was designed, its optimal composition was determined, and the frost-resistance and water-absorption parameters were evaluated. The composition material containing 5–10 wt. % of the mineral residue after the thermal treatment of OBMC is optimal.

Thus, as a result of our research, a technology of thermal destruction of OBMC at temperatures below 340°C has been designed, and the resulted solid residue has been used as a mineral component of an asphaltic concrete composition.

UNEXPECTED FEATURE OF HOMOGENEOUS REACTIONS – C_9-C_{12} ALKYNES CARBONYLATION

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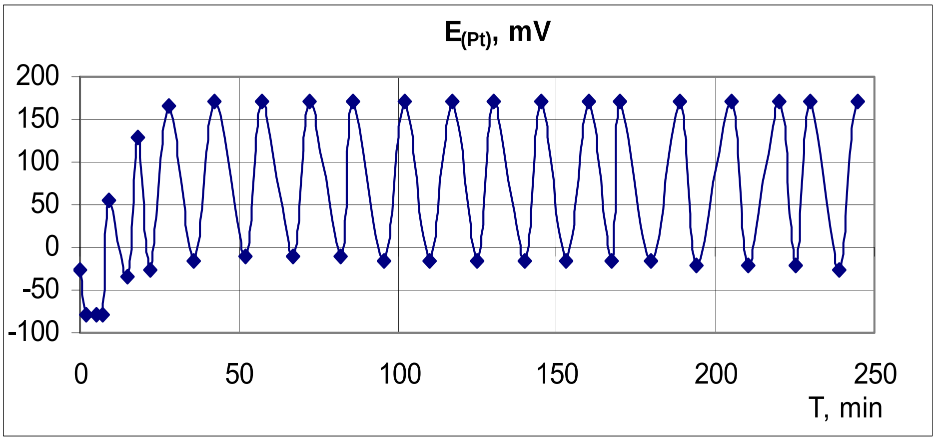
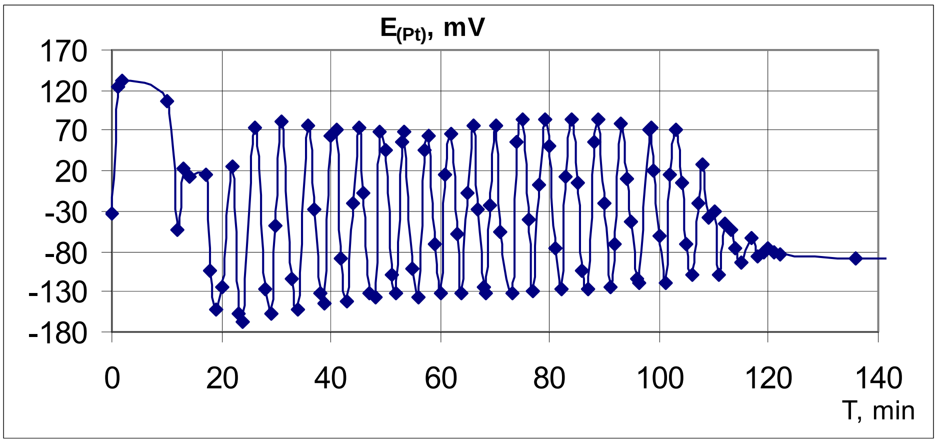
The oscillating reactions were discovered in many chemical and biological systems. The most part of oscillatory homogeneous reactions investigated in chemistry are processes of organic substrate oxidation by strong oxidants [1].

For several years in MITHT investigations of oscillating modes of the oxidative carbonylation reactions in homogeneous catalysis by metal complex in alcohol solutions of palladium salts with various organic substrates were conducted. We have showed that the phenomenon of oscillations can be observed for reactions with participation of different alkynes, and also in different catalytic systems, for example, in system $PdBr_2$ - LiBr, in which the occurrence of chaotic oscillations was demonstrated.



Oxidative carbonylation of methylacetylene.
$[PdI_2]_0$ = 0,01 M; $[KI]_0$ = 0,4 M; $[CH_3C{\equiv}CH]_0 : [CO]_0 : [O_2]_0 = 5 : 3 : 2$; P_{tot} = 1 atm

The modes of developed oscillations in reactions involving phenyl- and methyl acetylene, 2-methyl-3-butin-2-ol, 2-propin-1-ol in the systems PdI_2-KI-CO-O_2-CH_3OH; $PdBr_2$-LiBr-CO-O_2-CH_3OH; $PdBr_2$-LiBr-CO-O_2-$(CH_3)_2CO$-H_2O have been found [2-5]. Recently interesting modes of oscillations in carbonylation reactions of 1-nonin, 1-decin and 1-dodecin in the system PdI_2-KI-CO-O_2-CH_3OH were found with a number of features depending on the nature of the substrate.



Oscillating mode of 1-nonyne oxidative carbonylation reaction
$[KI]_0$ = 0,4 M**;** $[PdI_2]_0$ = 0,01 M**;** $[\text{1-nonyne}]_0$ = 0,1 M**;**
$[CO]_0$ **:** $[O_2]_0$ = 3 **:** 2, V_{CH3OH} = 10 mL

The study of mechanisms of some other processes in organometallic catalysis allows us to expect occurrence of self-oscillations and other critical phenomena. The searching for such phenomena is important for development of the theory of catalytic reaction mechanisms. The presence of oscillations, besides, is the powerful tool of the mechanistic hypotheses discrimination.

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POSSIBILITY OF DETERMINING OF SIZES OF NANOOBJECTS IN POROUS CATALYSTS AND ADSORBENTS ON A METHOD OF PAS

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It is known [1] that the positrons are effectively probing the free volume of nano-objects with dimensions in the angstrom and nanometer ranges in metals and alloys, and semiconductors and porous systems. Of particular importance is the possibility of determining the size of nano-objects in porous catalysts and adsorbents in projects of catalytic reactors. This requires comprehensive studies of the defect and porous structure of catalysts materials containing nanometer-sized cavity (vacancies, vacancy clusters, pores) using different methods of positron annihilation spectroscopy (PAS). This will set the connection between the experimentally measured parameters of the annihilation spectra and characteristics nanoobjects (type, size, concentration) in these materials. The behavior of nanometer objects is very important. Performing this kind of research will contribute to the accumulation of basic knowledge about porous structure of catalysts materials, development of theoretical models describing the properties and behavior of nanoscale defects. It is shown that one of the most effective methods for determining the average size $\overline{R}$ of cylindrical and spherical nano-objects (the free volume of pores, cavities, voids, etc.), their average values of concentration $\overline{N}$ and chemical composition at the site of positron annihilation in porous systems and some of the defective materials (and in a large number of technologically important materials and in porous catalysts and adsorbents) is a method of positron annihilation spectroscopy (PAS) [1-3]. This allows to determine the average values $\overline{V}_{rad} = (4/3)\pi\overline{R}^3\overline{N}$ of percentage of free space formed in in porous catalysts and adsorbents of catalytical technology in their operation. We discuss the idea of searching for correlations between the values $\overline{V}_{rad} = (4/3)\pi\overline{R}^3\overline{N}$ and mechanical and catalitical properties of materials, for example, their values of selectivity and catalytic activity. A brief review of experimental studies of nano-objects in porous materials of various grades are used as structural materials in modern porous catalysts and adsorbents may confirm these assumptions. An important role is played by the experimental methods for determining of properties porous catalysts and adsorbents. Particular importance is the search for critical defects, strongly violating the mechanical and catalitical properties.

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DEVELOPMENT AND MATHEMATICAL MODELING OF THE PROCESS HYDROGENATION OF ETHYL-VINILACETYLENE FRACTION

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Conserve energy, waste production and further use of the processed products are current and future tasks. At the moment, the plant "Ethylene" association "Nizhnekamskneftekhim" in the production of 1,3-butadiene by extractive distillation by-products adverse acetylene gases concentrate (ethyl-vinilacetylene fraction) in an amount up to 1 ton per hour (8000 tons per year), containing up to 30 wt % of acetylene impurities, 43 wt % of olefins and to 7 wt % of 1,3-butadiene. Due to high concentration and the absence of vinylacetylene at the plant "Ethylene" the process of refining a given fraction adverse gases are burned in the flame.

Reducing energy consumption of the process and increasing the yield of 1,3-butadiene is possible with the process of hydrogenation in the presence of a palladium on alumina catalyst.

The implementation process of hydrogenation of ethyl-vinilacetylene concentrate will eliminate flaring of hydrocarbons and subsequent stock return in the process of separation by extractive distillation hydrogenation products - 1,3-butadiene and butenes normal and iso-butane structure.

The aim is to develop and mathematical modeling the technological scheme of hydrogenation of ethyl-vinilacetylene concentrate in the presence of a palladium on alumina catalyst.

Using data from the pilot test the model set in an industrial environment mathematical modeling and calculation of technological apparatus: an adsorber, reactors, jet ejector gas developed a technological scheme (figure 1) of gas-phase hydrogenation process vinilacetylene impurities in ethyl-vinilacetylene fraction on palladium catalyst with dilution of ethyl-vinilacetylene concentrate recycle flow hydrogenation and subsequent return of the hydrogenation products in the technological scheme of separation of 1,3-butadiene by extractive distillation. This technological scheme is planned for introduction at the plant "Ethylene," association "Nizhnekamskneftekhim".

The technological scheme (figure 1) of the apparatus consists of nodes: drying the concentrate in the adsorbers, hydrogenation of concentrate in the reactors, the collection and separation of hydrogenation in the sump, drying and regeneration of the adsorbent, dehydration and regeneration of the catalyst.

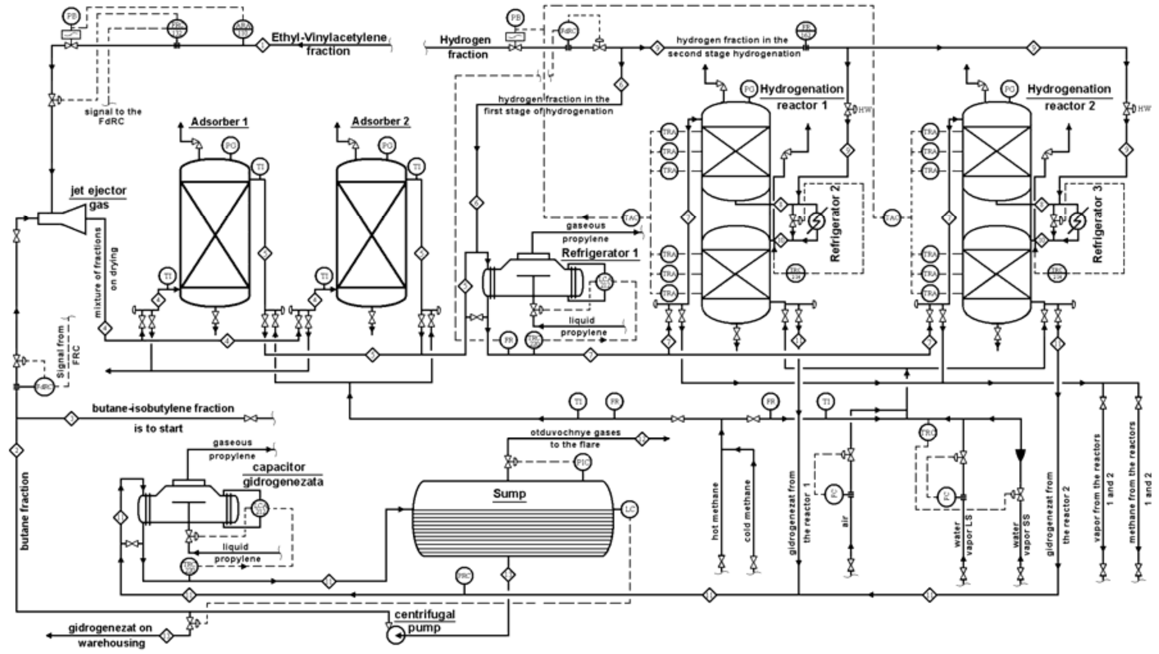

Figure 1 - The technological scheme of the hydrogenation ethyl-vinilacetylene fraction

The technological scheme takes into account dilution of ethyl-vinilacetylene concentrate recycle flow hydrogenation using a jet ejector gas and the subsequent return of the hydrogenation products in the technological scheme of separation of 1,3-butadiene by extractive distillation.

As a result of this scheme can be ensured access to an additional 1,3-butadiene in an amount of up to 1700 tons per year, or butenes to 6500 tons per year or butane to 7500 tons per year.

SPECIAL FEATURES OF OXIDATIVE CHLORATION STAGE FOR REFORMING PLATINUM CATALYSTS AT INDUSTRIAL INSTALLATION

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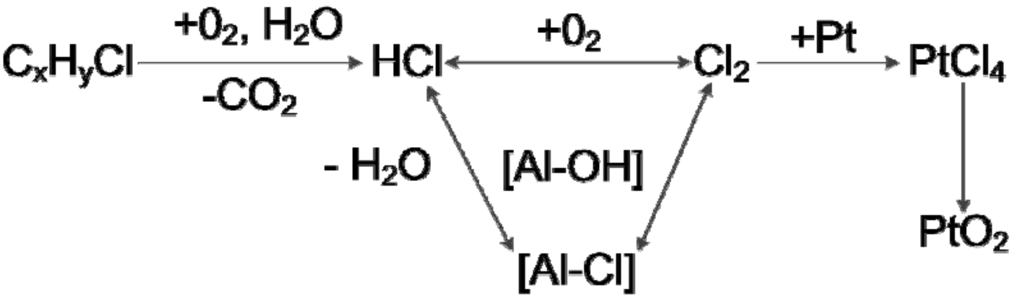
Catalytic reforming is basic process for high-octane compounds in Russian Federation. Dispersed platinum on a γ-Al_2O_3 carrier is a catalyst for process. During operation cycle of reforming installation catalyst is getting deactivated, so it is needed to regenerate catalyst activity. Length of next operation cycle depends on quality of reactivation. Stage of oxidative chloration takes the main influence on it [1].

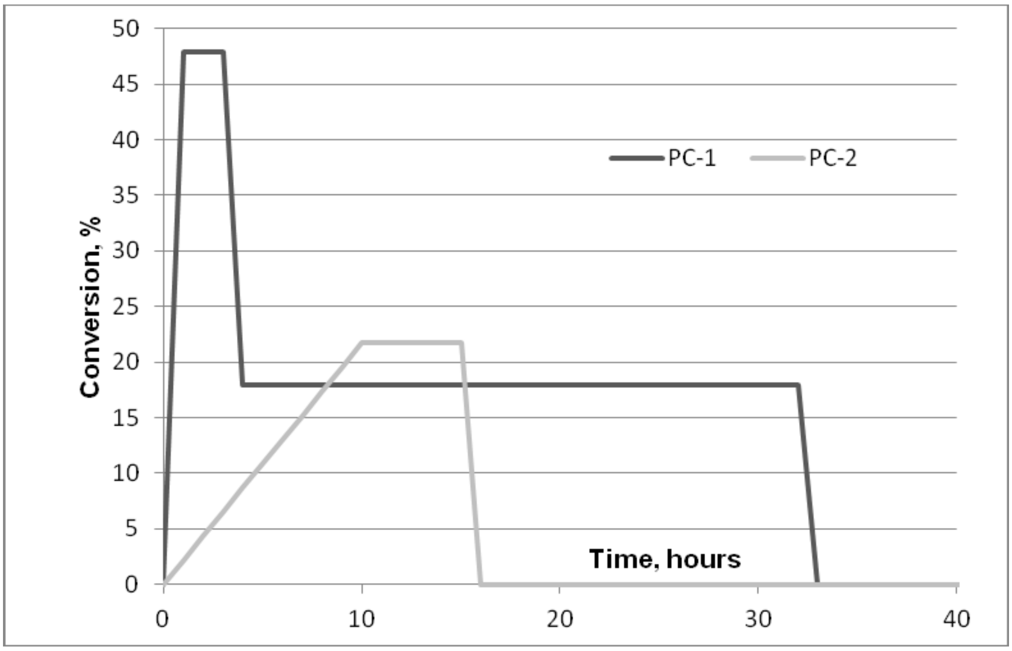
This research is aimed for analysis of oxidative chloration stage for different reforming catalysts. Scheme of chemical reactions at catalyst surface is presented at pic. 1.



Picture 1. Scheme of chemical reactions at oxidative chloration stage.

As it seen, platinum interacts with Cl_2 only, so one of parameters that should be controlled is conversion of hydrogen chloride to chlorine. When the highest possible temperatures of stage (510-520 °C) is reached, conversion should be controlled by content of oxygen in an air flow, the higher the content, the higher the conversion. The maximum oxygen contend is about 12 % vol. Required conversion for two types of catalysts (PC-1 and PC-2) was calculated with application of mathematical model of oxidative chloration stage [2].

Catalyst PC-1 requires increased conversion (up to 50 %) for 4-5 hours at the beginning of stage. After it is needed to keep lower conversion (20 % approx.) for 30 hours. For catalyst PC-2 it is needed to gradually increase air flow temperature (to 510 °C) and oxygen content (to 10 % vol.), so it causes increasing of conversion up to 25 %. This conditions should be kept for 6-8 hours. In some cases it is also recommended to increase conversion by higher rate of chlorine chemical.



Picture 2. Required conversion at oxidative chloration stage for PC-1 and PC-2 catalysts.

Deviation between real and required parameters of process causes redispersion of platinum at non-optimal conditions. So it decrease the length of operation cycle and the number of regenerations. That's why so important to determine parameters of oxidative chloration properly.

Different catalysts require different parameters of oxidative chloration because of different ways of obtaining.

Quality of catalyst reactivation depends on conditions of oxidative chloration stage. The last should be different for different types of catalysts and be under control during the whole stage. Mathematical model of oxidative chloration allows to improve quality of catalyst regeneration and determine optimal operating conditions.

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DEVELOPMENT OF NEW REACTORS FOR CHANGED OBJECTIVES OF PETROLEUM REFINING INDUSTRY

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Structural changes occurring currently in the global chemical and petrochemical market have influenced on redistribution of capacities over various regions of our planet and resulted in reducing a total capacity of the global oil-refining industry in 2011. First of all, the aftermath of the global economic crisis continues to affect economies of the USA and West Europe. It is in these regions that 7 refineries were closed and production capacities reduced more than by 280,000 bpsd during the last year. On the contrary, in Asia and the Middle East the production capacity increased more than by 76,000 bpsd. A certain global recession in the oil-refining industry should be labeled as a temporary problem. A multitude of new refineries, being now at various stages of design, construction and modernization, will be put into operation in the next few years, for the most part in South-East Asia and the Middle East, which will result in the global rearrangement of streams of raw materials and products.

Along with toughening of environmental standards for modern fuels and increasing a share of petrochemical feedstock in the total output, a percentage of heavy and residue refinery feedstock is rising, which is favorable for the implementation of high-technology destructive catalytic and hydrogenation processes.

In Russia, one of the important aspects of modernization is the improvement of a crude oil conversion level on the background of an increase in crude oil production up to 510 million ton in 2011. This problem is becoming increasingly urgent due to a drastic restriction of market niche for Russian fuel oil producers in Europe.

It is noted that up-to-date processes and technologies for producing fuels for cold and arctic climates need to be actively introduced in Russia. These tasks will be achieved by means of the construction of two-step cracking units, state-of-the-art hydrotreating / hydroisomerization units and the conversion of diesel fuel hydrotreating units into hydrodewaxing units, which would require modifications in the reactor design and process flow diagrams of the units..

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Currently, one of the important problems in producing high-octane gasoline components is the low quality of catalytically cracked gasoline. Of particular interest are advanced reaction columns offered by CD Tech for catalytically cracked gasoline cut hydrotreating blocks.

Heavy crude oil and residue processing, combination of fuel and petrochemical (producing gasoline, diesel fuel and propylene) configurations, and feed-catalyst contact time reducing are advanced trends in the catalytic cracking process evolution. Promising designs of reactor-regenerator blocks of catalytic crackers, including KBR’s Maxofin and UOP’s Millisecond, are reviewed.

The main trends in the evolution of the catalytic hydrocracking are discussed, including an increased liquid product yield and realization of the process in a three-phase moving catalyst bed. A promising technology of heavy petroleum residue hydroconversion developed by the RAS Institute of Petrochemical Synthesis is reviewed. Basic features of this technology are described, namely, use of nanocatalysts, average pressure of 7 to 8 MPa, a conversion level of 90 to 92% and a high flexibility in respect of product yields. Hydroconversion reactors are compared with other global technologies such as H-Oil (Axens), LC-Fining (Chevron Lummus Global), Uniflex (UOP) and heavy residue hydrocracking (ENI) processes.

MATHEMATICAL SIMULATION OF A FLUIDIZED BED CATALYST IN THE ISOBUTANE DEHYDROGENATION REACTOR

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In order to optimize the operation of the isobutane dehydrogenation reactor with a fluidized bed of chromia-alumina catalyst, in particular for the organization of a uniform distribution of catalyst in the cross section and height of the reactor, reducing the entrainment of fine particles, to maintain the necessary level of catalyst, mathematical simulation of a fluidized bed was carried out. It was investigated the motion of solid catalyst particles with a size of 20-200 microns in isobutane dehydrogenation reactor of JSC "Nizhnekamskneftekhim", which had an internal diameter of 5.1 m and 17.4 m in height, was partitioned by ten distributive lattice of angle-type with an area of free section of 30%.

A calculation was performed for the periodic two-dimensional flow reactor section which is 0.432 m in width with six sections of the distributive lattice. A simulation was carried out for the following boundary conditions: the right and left borders are periodic, velocity-inlet condition for the gas and impermeability condition for the catalyst at the bottom of the reactor. Simulation of multiphase flow was carried out by using Eulerian-Eulerian approach.

Figure 1a shows a calculated the catalyst concentration field with a particle size of 100 microns in diameter at a fixed time. At the entrance of the reactor large rarefied zones were formed. Between the lattices the average concentration of the solid phase was equalized, and the zones with catalyst accumulation at the lattices are observed. Calculations showed that at any given time approximately two thirds of the lattice is locked to by the catalyst that falls down. Through the rest of the free cross section the gas bubbles go up.

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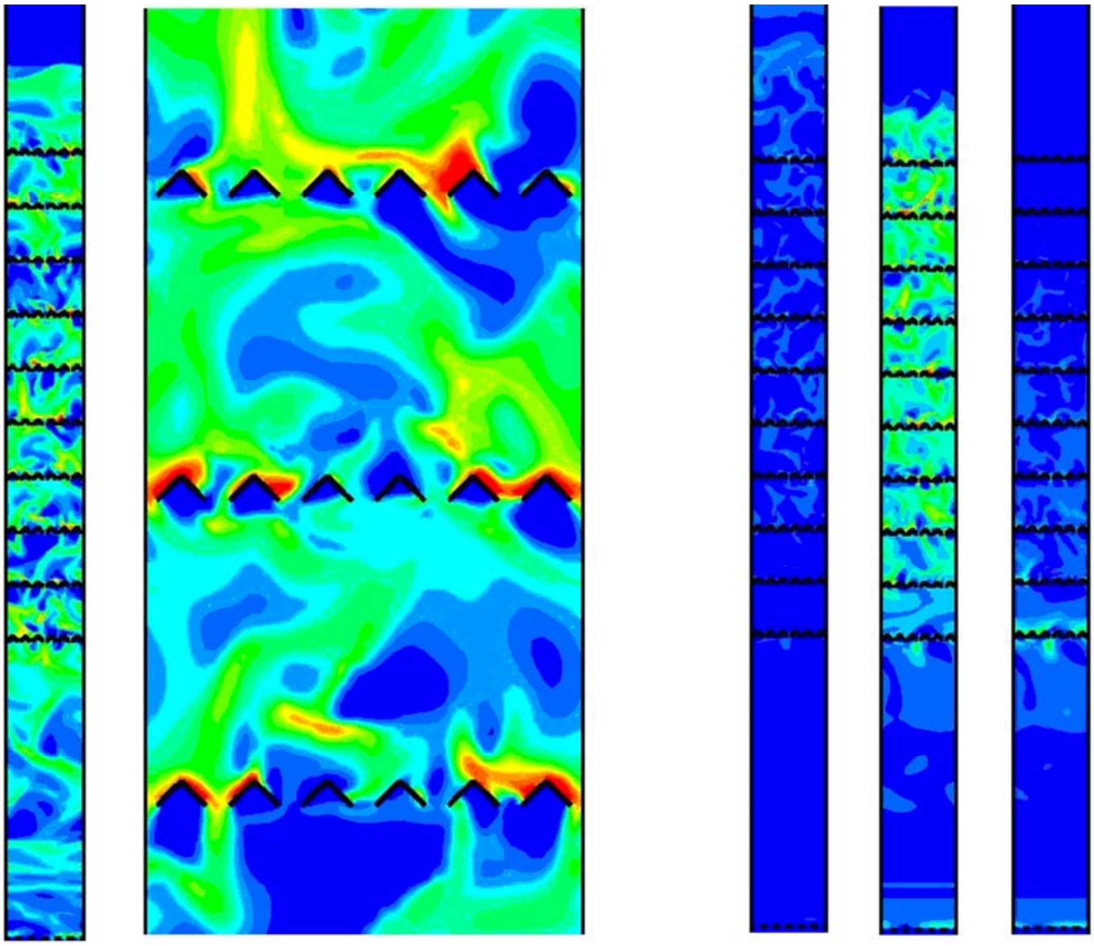

a b

Figure 1. The distribution of the catalyst in the cross section of the model reactor

Figure 1b shows the distribution of catalyst with the particle size of 50, 100 and 150 microns in diameter. Particles with a size of 50 microns (left) are entrained by gas flow in the upper part of the reactor. Particles of intermediate size (center) is uniformly distributed in the reactor between the lattices. Large particles (right) are concentrated mainly near the first lattice.

Based on these results a mathematical model was developed which allows to predict the behavior of polydisperse catalyst bed.

METHANE CONVERSION INTO AROMATIC HYDROCARBONS OVER Ag-Mo/ZSM-5 CATALYSTS

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Methane dehydroaromatization under nonoxidative conditions on zeolite catalysts modified with transition metal ions is a promising process for the efficient utilization of natural gas and casing-head gas. A significant drawback of these catalysts is their rapid deactivation under the severe conditions of the process. To increase the time of stable catalyst in methane dehydroaromatization, the catalysts are modified with various metals (Y, Zr, La, Pt and Ni) [1-2]. In this work, we study the modifying effect of silver on the catalytic proerties of molybdenum-conaining zeolite ZSM-5 during a methane dehydroaromatization reaction. The microstructure and composition of Ag-Mo/ZSM-5 catalists are studied by high-resolution transmission electron microscopy and energy dispersive X-ray analysis.

Catalysts were prepared by mechanically mixing zeolite ZSM-5 with the molar ratio SiO_2/Al_2O_3 = 50 and the nanosized powders of Mo and Ag in a KM-1 vibratory ball mill (Germany) for 4 h. Thereafter, the resulting mixtures were calcined at 540°C for 4 h. The nanopopowders of Mo and Ag were prepared by the method of electrical explosion of wires in an atmosphere of argon. The concentration of Mo in the zeolite was 4.0 wt%, and the concentration of Ag in the 4.0% Mo/ZSM-5 catalytic system was varied from 0.1 to 2.0 wt%. The nonoxidative conversion of methane (99.99% purity) was performed in a flow setup at 750°C and atmospheric pressure, methane was supplied at a space velocity of 1000 h^{-1}. HR TEM images were obtained in a JEM-2010 electron microscope (JEOL, Japan) with a image resolution of 0.14 nm at an accelerating voltage of 200 kV. The high-resolution images of uniform structure were analyzed using the Fourier analysis. Local elemental composition of the samples was determined by the energy-dispersive X-ray analysis (EDX) in an EDAX spectrometer (EDAX Co.) equipped with a Si(Li) detector with an energy resolution of no worse than 130 eV. The samples for HR TEM were prepared on perforated carbon substrates fixed on copper gauzes.

V-31

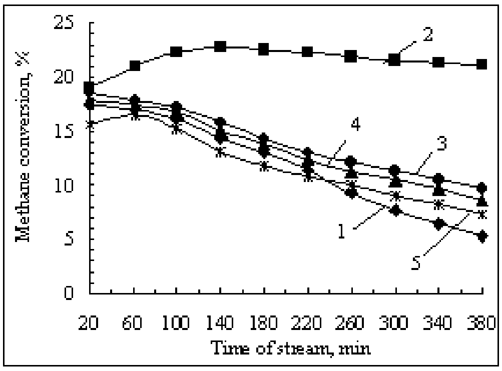

Figure 1: Dependence of the conversion of methane on the time of methane de-hydroaromatization on Mo/ZSM-5 with various silver nanopowder contents: (1) initial 4.0% Mo/ZSM-5 and (2) 0.1, (3) 0.5, (4) 1.0, or (5) 2.0% Ag (T = 750°C; GHSV = 1000 h^{-1}).

It has been found out that the 4.0% Mo/ZSM-5 catalysts modified with nanosized Ag powder ensures much higher methane conversion, better selectivity of hydrocarbons and higher yields of benzene and naphthalene. Figure 1 illustrates the effects of the concentration of the nanosized Ag powder and the reaction time of methane dehydroaromatization on the methane conversion and the stability of catalysts. The highest methane conversion was achieved by adding 0.1% of Ag nanopowder. After the induction period the conversion is maximal and reaches the value of more than 22% using the catalyst sample, containing 0.1% Ag-4.0% Mo/ZSM-5, that is 6% higher when using Mo/ZSM-5. Furthermore, the methane conversion ratio over the 0.1% Ag-4.0% Mo/ZSM-5 catalyst for 380 min of operation decreased by 1.7%, whereas that over the initial sample – by 12.1%. The selectivity of aromatic hydrocarbon formation over the Ag-Mo-containing zeolite was found to be as high as 80%. When the amount of Ag in Mo/ZSM-5 was increased to 0.5% and higher, less active and stable catalysts were obtained compared to the 0.1% Ag-4.0% Mo/ZSM-5 sample.

It, apparently, is connected with blocking by agglomerates of silver of active superficial centres Mo_2C formed during reaction and zeolite channels in which are localised molybdenum clusters and the acid centres of the zeolite are located. Data HR TEM and EDX-spectroscopy confirms presence of silver at structure carbiding particles of molybdenum and in the form of units of the micron sizes. Thus, we can conclude that the Mo-containing zeolite ZSM-5 with the addition of 0.1% Ag nanopowder is superior to other samples in not only catalytic activity but also stability.

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QUANTUM-MECHANICAL SEARCH FOR REACTION KINETIC MECHANISM

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In order to understand the fundamental mechanism of combustion processes during inhibition by chemical active substances, it is necessary to measure the concentrations of all the species throughout the flame front. Many of authors have determined the kinetic parameters of the elementary reactions taking place in the combustion of hydrogen-oxygen mixtures with adding of phosphorus containing fire extinguishing compounds, using different techniques. However, because of the large variety of species present in flames and therefore the numerous ways in which they interact, only a few studies have been devoted to the detailed analysis.

In connection with the problem of flame inhibition by trymetylphosphate (TMP) and dimethyl methyl phosphonate (DMMP) was applied molecular-beam masspectrometry for investigation of bunzen flame. In this flame radicals were detected HPO_2•, PO_2•, PO• [1]. It was assumed that these particles are involved in inhibiting of combustion process. Chemically active flame inhibitors affect the rate of combustion by catalytic recombination of key flame radicals in particular H• and O•• atoms and hydroxyl radicals. This conclusion is confirmed Twarowski mechanism [2-4]. But unfortunately more thorough explanation of the mechanism of catalytic effect of TMP and DMMP on hydrogen flame does not occur in most experimental work. Moreover, among the various mechanisms are significant differences. Thus, according to the mechanism [5] the main reaction path of destruction DMMP is following: $(CH_3)(CH_3O)_2PO \rightarrow (CH_2O)(CH_3O)(CH_3)PO \rightarrow (H)(CH_3O)_2(CH_3)PO \rightarrow (CH_3O)(CH_3)PO \rightarrow (CH_3PO_2)$. Convert DMMP by methyl phosphonates leads to CH_3PO_2. Next CH_3PO_2 reaction forms phosphorus and products HOPO•, $HOPO_2$, PO_2•, PO•. In the kinetic model [6] is the main way through which methyl phosphonates leads to the formation orthophosphate acid $(HO)_3PO$, which was discovered by them in significant quantities in the reaction mixture. The final products of transformation are similar. Thus, the experimenters cannot give unanimous answers relatively important intermediate: CH_3PO_2 or $(HO)_3PO$. The quantum-mechanical ab initio calculations in the basis 6-31G* of energy chemical transformations on both mechanisms carried out to clarify kinetic mechanism (table).

Table. The destruction energy of bonds in the TMP molecule and interaction energy of formed products with active centers of flame, calculated by ab initio calculations in the basis 6-31G*

The reaction ways	Destruction (interaction) energy, kcal/mol		
$CH_3O\text{-}OP(OCH_3)_2 \rightarrow CH_3O\bullet + OP(OCH_3)_2\bullet$	35,07		
$CH_3O\text{-}OP(OCH_3)_2 \rightarrow CH_3\bullet + OOP(OCH_3)_2\bullet$	64.25		
$CH_3O\text{-}OP(OCH_3)_2 + OH\bullet \rightarrow CH_2O\text{-}OP(OCH_3)_2\bullet + H_2O$	51.32		
$CH_3O\text{-}OP(OCH_3)_2 + H\bullet \rightarrow CH_2O\text{-}OP(OCH_3)_2\bullet + H_2$	41,41		
Active centers of flame Destruction products	H•	O•	•OH
$OP(OCH_3)\bullet$	39,78	1,44	30,93
$CH_3O\bullet$	74,61	23,4	11,05

Kinetic model of Werner and Cool could not be verified in such a way that the authors had no quantifiable concentrations of these particles, mainly phosphoric acid and phosphorus oxides [5]. There is another view of the mechanism of transformation TMP in flames. Literary data on the study of chemistry of phosphorus compounds show that for the study of the real reaction towards their interaction with radicals and intermediate compounds in the hydrogen flame, be aware transformation TMP under the influence of active centers of flame (O•, H•, OH•) [6]. As we can see from the calculation results (table) according to our research the Korobeinichev's mechanism is more energetically preferable.

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WAYS FOR DEVELOPING ENERGY- AND RESOURCES-SAVING TECHNOLOGIES ON THE BASIS OF SYSTEM UNITY OF CHEMICAL CONVERSION AND MIXTURE SEPARATION PROCESSES

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This paper presents some results of the development of a methodology and practical techniques for designing energy- and resources-saving chemical technologies on the basis of system unity of the processes of chemical conversion and mixture separation. In practice, the development of complex technological processes is often conducted in the sequence at which a technology for chemical conversion is first developed and only then a technology for separation is developed. This frequently leads to serious errors and necessity of the subsequent fundamental changes in the process because of arising difficulties during separation. For example, to produce high-octane methyl-tert-butyl ether from tert-butanol and methanol, Huntsman (USA) took a route of direct chemical reaction of these alcohols [Pat. US 5856588]. This led to the production of the reaction mixture with numerous azeotropes impeding mixture separation by rectification. Our analysis has shown that the initial dehydration of tert-butanol and then combining isobutene with methanol make it possible to obtain the product at 3–3.5 times lower energy consumption. A large number of such examples can be given.

In developing energy-saving chemical engineering schemes of production, it is necessary to take into account thermodynamic, kinetic and technological factors limiting the values of conversion degree and selectivity, as well as factors complicating the separation of mixture components. Positive possibilities revealed in due time in separating mixtures can lead to simplification and increase in the efficiency of the processes of chemical conversions. The proposed approach requires the simultaneous study of the processes of chemical conversions and separation of the formed mixture, beginning from a laboratory level. Analysis of the variants of flow diagrams of some petrochemical processes was performed in order to find an efficient variant without using long standard procedures. The generation of various variants of flow diagrams was conducted on the basis of plant (the characteristic compositions of fractions, requirements on the quality of a product with respect to impurity content, pressure and temperature ranges, reflux-to-product ratios) and laboratory experimental data (azeotropy, phase and chemical equilibria, kinetic data). The specificity of the developed approach is that the variants of flow diagrams were considered that included not only various configurations of a separation unit, but also the variations of chemical stages of the implementation of a process in order to eliminate arising difficulties and thermodynamic limitations during separation. In each case, the expediency of the use of hybrid processes (catalytic distillation, extractive rectification) in the implementation of the productions under study was considered.

The production of pure 1-butene from butane–n-butene C4-fractions was analyzed. The proposed variant of a flow diagram obtained on the basis of an express analysis makes it possible to evaporate in a column still 4.5 times smaller quantity of the mixture being separated as compared with operating enterprises. Besides, the degree of the use of n-butenes for producing pure 1-butene reaches 97-98%; i.e., at the same quantity of a feedstock 1.5 times larger amount of a product can be manufactured. Finally, the diameter of distillation columns decreased to 3.6 m, instead of 7-7.5 m, which makes it possible to transport them by rail. Analysis of the extraction of pure isobutene from C4-fractions is also performed, and a flow diagram is developed that makes it possible to decrease power consumption per 1 ton of pure isobutane by a factor of 6 down to 2.1 GJ, instead of 12.6 GJ in a commercial process.

This work was supported by the Russian Foundation for Basic Research (project no. 11-03-01015).

MATHEMATICAL SIMULATION OF ISOAMYLENE DEHYDROGENATION REACTOR HYDRODYNAMICS AND GAS DISTRIBUTING DEVICE UPGRADE (MIXER)

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The commercial process of dehydrogenation of isoamylenes to isoprene occurs in adiabatic reactors with a fixed granular bed of catalyst. The dehydrogenation is an endothermic opposing reaction which is accompanied with an increase in volume due to the hydrogen release. The process occurs in the presence of water vapor to supply heat to the reaction zone and decrease partial pressure. Dehydrogenation reactor of isoamylene to isoprene is a complex technical unit. The gas distributing device, providing the feeding of isoamylene and water vapor to the upper gas chamber, is installed at the top of the reactor. After that the mixture of isoamylene and water vapor is filtered through the fixed bed of iron-potassium catalyst. Here the chemical reactions occur which result in isoprene production. It is clear that the reactor output depends mainly on mixing quality of isoamylene and vapor. The system of horizontal, conical, and perforated plates is provided for improving the mixing process. It is in the bottom of the gas distributing device.

For the definition of efficiency of gas distributing device the mathematical simulation of thermal hydrodynamic processes in the reactor was carried out using CFD Fluent-Gambit 6.0 software package.

It is determined that hot vapor flows around the feeding pipe and goes down to the gas chamber, deviated ahead from its axis. Herewith it forces the cold flow out of the axis to the inlet side of the pipe for vapor supply. Therefore, the construction of gas distributor used in the reactor does not provide uniform distribution of temperatures and concentrations of isoamylenes.

The upgrade of the gas distributing device can improve the quality of mixing. The perforation of the feeding pipe provides intensive uniform mixing.

It leads to substantial equalizing of thermal hydrodynamic parameters of the mixture in the premixing chamber. When vapor-gas mixture of the main line, the cascade of diverting plates, and the upper gas chamber passes on, the mixture parameters will undergo final equalization. Finally when the mixture enters the granular bed of catalyst the mixing quality will be characterized by lower nonuniformity of temperature field.

The work was done in association with Ministry of the Russian Federation.

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A CATALYTIC HEAT GENERATOR FOR WASTE PROCESSING

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Due to the permanent aggravation of hydrocarbon fuel deficit on our planet and the catastrophic environmental status of the atmosphere, novel solutions of the problem of burning process optimization for every kind of fuel and the usage of alternative power sources become rather topical.

Fuel combustion optimization implies the design of efficient techniques of combustion and reduced atmosphere contamination with harmful products.

The present work develops a catalytic heat-generation device for stages oxidation of any kind of fuel and organic waste processing on the basis of the results of our comprehensive studies in the field of environmentally-pure technologies of oxidation of organic substances, studies of physicochemical mechanisms of the reactions proceeding when fuel and wastes burn.

The development belongs to the engineering of heat energy generation on the principle of flameless catalytic fuel oxidation and can be used in industry, agriculture, transport, housing and communal services for autonomous water heating, air heating, and hot water supply for living and industrial premises.

Our catalytic heat-generating device can consume various kinds of fuel of any moisture content (natural gas, turf, firewood, wood chips, twigs, sawdust, industrial and household wastes).

The high efficiency of our heat generator is due to the conversion of fuel and its semiproducts in the presence of a heterogeneous catalyst.

Flameless catalytic combustion is a promising way of raising the efficiency of fuel combustion and harmful waste reduction. In the process of burning, fuel oxidation reactions proceed on the catalyst surface at relatively low temperatures to provide full fuel conversion with no nitrogen oxides formed and an efficient heat output.

In contrast to flame-torch fuel burning which proceeds according to the fast reaction of deep fuel oxidation to form carbon dioxide and water $CH_4+2O_2=CO_2+2H_2O$, incomplete fuel oxidation first goes in our catalytic heat generator to form carbon (II) oxide and hydrogen by the exothermic reaction $CH_4 + 0.5\ O2 \leftrightarrow CO + 2H_2$. The carbon oxide formed can react with water vapors to complete its oxidation to CO_2 to form hydrogen and additional heat.

Concurrently, the reaction $CO+3H_2=C_xH_y+H_2O$ proceeds to form a hydrocarbon, a source of extra heat amount at oxidation.

The gas composition in the combustion zone, and, hence, the heat effect of fuel gasification, are determined by the activity of the catalyst used, the oxygen concentration in the furnace, and the fuel combustion zone sizes, which is taken into account in our modeling of the offered device. The role of the catalyst is in redistribution of the main reaction of fuel combustion and catalytic purification of the waste gases.

The catalyst for fuel burning contains a thermostable porous carrier with active metal (copper and nickel) oxides deposited on it. Heat output from the generator can be implemented in various ways with the usage of a water or air heat carrier.

The catalytic heat generator with water heat removal is incorporated into the existing system of water heating; the maximum outlet water temperature is 95°C under natural circulation. For premises with no water heating system, devices with air heat removal are produced. A version of the heat generator is possible for operation with solid, liquid, and gaseous fuel. The device is supplied with a gas burner with a fuel supply channel. Any model of the catalytic heat generator is made of 5 to 1000 kW power. On the average, for heating of 10 m^2 premises, depending on their height, the power of 1.0–1.5 kW is enough.

The catalytic heat generator comprises a vertically-oriented case with an entrance for fuel supply and an output for waste gases, with two or three chambers, namely, a burning chamber in the lower part of the case and an above-located chamber of after-burning, grids with an immobile catalyst layer located in the chambers, a regulated air supply block in the lower part of the burning chamber; a channel of secondary air supply to the after-burning chamber; and a heat-exchange block. A high fire and explosion safety of the device is achieved due to the usage of the air supply block of original design.

Therefore, multistage combustion, the low-temperature and long mode of burning (8–20 h per fuel loading), a reduced air excess coefficient, and partial recirculation of combustion products provide the environmental purity and high efficiency of our heat generator. This model can be used as a thermochemical utilizer of industrial and household wastes of various compositions as well as a heat generator. The presence of the catalyst enables the high heat gain and efficient purification of the wastes gases from toxic substances.

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HYDRODYNAMIC ANALYSIS OF THE REACTOR-FIBRIDATOR IN THE GAS-LIQUID POLYCONDENSATION

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Distinctive feature of a method gas-liquid polycondensation overlapping of chemical process polyamidirovaniya and physical process of formation of polyamides of various morphology in one device – a reactor-fibridator (Fig.).

The reactor-fibridator intended for reception is fat-aromatic polyamide fibrids, differs compactness, high efficiency and will consist of the chamber of generating of a gas phase and the reactionary chamber located above it [1]. Various designs of reactionary chambers which basic difference consists in means of input of a gas phase in the reactionary chamber are developed. Means of input is executed in the form of a bar with free section 25 of % (Fig.), or mouths with equivalent section [2].

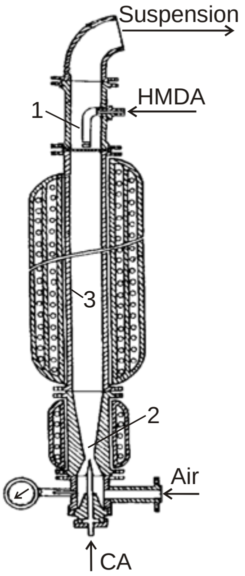
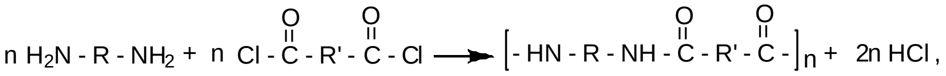


Fig. The reactor-fibridator

1 – reaction chamber;
2 – sprayer blender;
3 – evaporator-overheater;
CA – dicarboxylic acid dichlorides;
HMDA – hexamethylenediamine.

Described reactor apparatus should provide monomers polycondensation (1)



$$n\,H_2N-R-NH_2 + n\,Cl-\overset{\overset{O}{\|}}{C}-R'-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow \left[-HN-R-NH-\overset{\overset{O}{\|}}{C}-R'-\overset{\overset{O}{\|}}{C}-\right]_n + 2n\,HCl, \qquad (1)$$

low molecular products accepting and neutralization (2)

$$HCl + NaOH \longrightarrow NaCl + H_2O, \qquad (2)$$

as well as physical processes of polymer formation in fiber-film species (fibers) or gas structured elements with defined morphology and structure.

One of actual problems of development of technology polyamide fibrids gas-liquid polycondensation is optimization of the defining sizes of a reactor-fibridator, including internal diameter of the reactionary chamber. Experimental researches on studying influence of one of the basic technological parameters defining a foamy hydrodynamical mode of process and productivity of installation – linear speed of a gas phase (ω) on an output (ε_{CA}), the resulted viscosity (η) and degrees of a grinding (*DG*) polyamide fibrids, are executed in the specified two types of reactor the arrangements having the greatest internal diameters 16, 32, 50 and 100 mm.

Thus extreme functional dependences ε_{CA}, η, $DG = f(\omega)$, are revealed. It is necessary to note growth of optimum values of linear speed of a gas phase with an increase of diameter of the device in all investigated designs. However absolute values of optimum linear speed in the reactors-fibridators, differing means of input of a gas phase, do not coincide. In reactors without bars the big growth of optimum linear speed with an increase of diameter is observed. Consequently, productivity of the given type of reactors above, than at reactors-fibridators with bars. Advantage reactors without bars is also their higher operational reliability as it is not observed driving nonconsumable by solid particles oligoangidridov punching of a bar, and there is their ablation to reactionary weight.

Considering inapplicability of parameter «linear speed of a gas phase» as criterion of design the arrangements reactor's having different diameters and a design of means of input of a gas phase, it is lead the criterial analysis arrangements reactor's by two hydrodynamical criteria of similarity – Reynolds (*Re*) and Froude (*Fr*). At calculation of criterion of Reynolds correction for viscosity of a gas stream and was entered by variation of diameter of a reactor. For each investigated type of reactors uniform dependences are found ε_{CA}, η, $DG = f(Re)$, ε_{CA}, η, $DG = f(Fr)$ and optimum values of hydrodynamical criteria. Areas of optimum values depend both on diameter of a reactor-fibridator, and from molar parities monomers: at n_{DA}/n_{CA}=1,76-1,80 and *d*=16 mm *Re*=7000-8000, *Fr*=13000-17000; at n_{DA}/n_{CA}=1,15-1,50 and *d*=50 mm *Re*=13000-18000, *Fr*=7000-11000.

Found the criterial dependences allow to model processes gas-liquid polycondensation at synthesis aliphatic-aromatic polyamide fibrids, proceeding in an intensive foamy mode, and on the set diameter of the device in view of its design features to define optimum linear speed and productivity of installation as a whole.

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PRODUCTION OF SUPER-PURE HYDROGEN IN REACTORS WITH MEMBRANE SEPARATION FOR FUEL-CELLS

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The present report focuses its attention exclusively on the new types of membrane reactors (MRs) employing the new types of membranes for hydrogen generation in portable and stationery versions of polymer electrolytic membrane (PEM) and allied fuel cells. The main catalytic hydrogen-generation processes and types of fuels used in hydrogen production for fuel cells are described. In particular, attention was focused on catalytic production of hydrogen from natural gas, methanol, diesel fuel, coal, ethanol and biomass. The energy efficiencies of different fuels are presented. The benefits of a hydrogen energy policy are the reduction of the greenhouse effect. In the last years interest in hydrogen as an energy carrier has significantly increased both for vehicle fuelling and stationary energy production from fuel cells.

High purity hydrogen could be produced via dense Pd-based MRs, which allows the simultaneous performance of both chemical reaction and mixture gas separation in the same device with respect to conventional process, consisting of a reactor unit in series with other hydrogen separation/purification units. Two different types of dense pin-hole free membrane (tubular and disc's), produced by cold-rolling and diffusion welding technique, reporting its geometric characteristics, material composition, permeability, separation factors are presented. The development of hyperfine composite membrane on different suggests is given.

Different constructions of catalytic membrane reformers were developed for vehicles and power plants. Along with well known MRs as fixed-bed and circulating fluidized-bed membrane reformers offered new types of MR such as Hybrid Absorbent-Membrane Reactor (HAMR) and MR-based air revitalization system (MARS).

MR is producing of super-pure hydrogen; the hydrogen is generating electricity in fuel cell; the fuel cell in addition to electricity is producing of water; the vapor of water is a sweep gas for removal of hydrogen from MR. The final target in application of MRs is the minimization of cost and volume of fuel processor. At the same time it's necessary to provide the high energy efficiency, compactness, the lower temperature of fuel conversion, the receipt of super-pure hydrogen in single-step.

A significant drawback of the known membranes is short operation life and the high cost of primary component – Pd. However, the advances in the development of hyperfine composite membranes on different supports suggest good prospects for introducing membrane technologies into future hydrogen energy.

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ESTERIFICATION OF ACETIC WITH ETHANOL WITH MORDENITE-TYPE ZEOLITE MEMBRANE

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Membrane reactor is expected to improve the level of esterification conversion, displacing equilibrium by selective removal of by-product, water. In this study, we performed a simulation study on the behavior of the membrane reactor for the esterification of acetic acid (AcOH) with ethanol as well as the experiments using mordenite-type zeolite membrane, in which mordenite is a kind of zeolite having both high stability in acidic media and hydrophilic nature. Recently, we successfully synthesized compact mordenite membrane [1], which selectively permeated and separated water from alcohol [2].

A compact mordenite membrane was prepared on the outer surface of an α-alumina tubular support by a secondary growth method, following the procedure described elsewhere [2]. The membrane tube was set inside a stainless steel module. A hundred milligram of solid acid catalyst, Amberlyst-15, was placed on the outer surface of membrane. The exposure area of zeolite membrane was 6.28 cm^2. The feed for the esterification consisted of an equimolar mixture of AcOH and ethanol (both 0.1 mol). The retentate was circulated at a flow rate of 1 mL min^{-1}. The permeate side of membrane was vacuumed during the esterification.

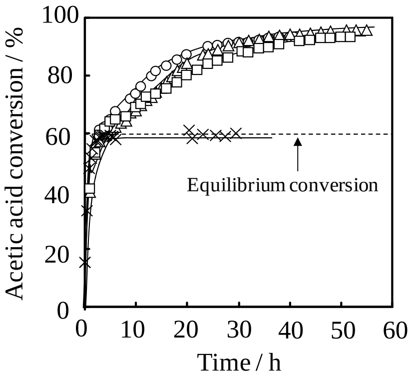

Fig. 1. Conversions of acetic acid as a function of reaction time at 403 K. Circle, 1st run; triangle, 2nd run; cubic, 3rd run; x, conventional reactor.

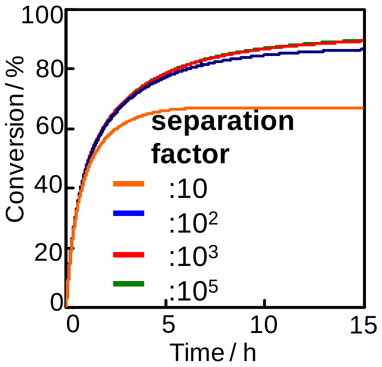

Fig. 2. Typical simulation results. Effect of separation factor of water/ ethanol on the conversion of AcOH. Reactor volume, 30 m^3; membrane area, 500 m^2 ; permeance : 1.0×10^{-6} mol m^{-2} s^{-1} Pa^{-1}, temperature : 403 K; reaction rate constant : 2.98×10^{-8} mol^{-1} m^3 s^{-1}.

Fig. 1 shows the experimental results of the esterification with the mordenite membrane at 403 K. Use of membrane increased the level of conversion from about 60 (equilibrium value) to >90 %. Repeated use of the membrane gave reproducible results.

In the simulation model, we integrated a perfectly-mixed batch reactor with a pervaporation unit. The expression of the rate of the esterification in the membrane reactor is controlled by both the rates of reaction and permeation. All the parameters for the simulation such as the rates of reaction and permeation were determined by the experiments: No fitting parameters were used. We confirmed that the simulation model developed in this study sufficiently explains the experimental results.

We carried out the sensitivity analysis of the model. Water removal from the reaction side contributed to improving the level of AcOH conversion by displacing the equilibrium. However, an increase of water permeance above 1.0×10^{-6} mol m^{-2} s^{-1} Pa^{-1} would not be effective to improve the level of conversion because the concentration of water in the reactor side is kept very low throughout the reaction.

The simulation was done with different separation factors, namely water/AcOH, water/ehanol and water/ethylacetate. When the separation factor of water against AcOH or ethanol was too small, the reacants passed through the membrane, resulting in a decrease of attainable level of conversion. Fig. 2 shows the effect of the water/ethanol selectivities on the level of the converiosn of AcOH. Similarly, when the separation factor of water against ethyl acetate was too small, the yield of ethyl acetate has a maximum with time course, because produced ethyl acetate was lost to the permeate side.

As a result, we concluded that separation factor should be larger than 100 for water/AcOH and water/ethanol, and larger than 1000 for water/ethyl acetate. Mordenite membrane developed satisfies such requirements for separation factors.

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Acknowledgement

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MATHEMATICAL MODELING AND STEADY STATES MULTIPLICITY ANALYSIS OF METHYL TERT-BUTYL ETHER REACTIVE DISTILLATION SYNTHESIS

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Reactive distillation is considered as a promising and economically sound way of the process realization in comparison with the conventional schemes. The reactive distillation is successfully implemented in a number of important chemical processes, for instance, syntheses of petrol additions, such as methyl tert-butyl ether (MTBE). Existence of steady states multiplicity with different outputs of desired product requires an effective control based on mathematical models, embedded in control algorithm [1]. Thereby, the aim of this work is to create a mathematical model of the reactive distillation MTBE production, which would be suitable for the precise process control, prediction of the synthesis behavior and stability analysis.

The basic chemical reaction of MTBE synthesis can be described by the following scheme [2]:

$$CH_3OH + CH_2{=}C(CH_3)_2 \leftrightarrow CH_3\text{-}O\text{-}C(CH_3)_3 + \Delta H_{ch.r} \qquad (1)$$

where $\Delta H_{ch.r.}$ – specific chemical reaction heat effect, kJ/kgmole.

In the developed equilibtium model concentration and temperature profiles for the reactive section of the column expressed through controllable and output variables.

Material balance:

$$\frac{1}{R+1}+\frac{1}{R+1}\cdot\frac{1}{(R+1)\cdot k_i}+\left[\frac{1}{R+1}\right]\cdot\left(\left[\frac{1}{R+1}\right]^2\frac{1}{k_i\cdot k_{i-1}}+\ldots+\left[\frac{1}{R+1}\right]^i\frac{1}{\prod\limits_{i=1}^{M}k_i}\right)-$$
$$-\frac{x_i}{x_d}+\frac{1}{x_d}\cdot\frac{U_i}{L_i}\sum_{\rho=1}^{m}v_{j,\rho}\cdot r_{i,\rho}=F_2^m(R) \qquad (2)$$

U_i – liquid holdup on the stage number i, kgmole/h; $v_{i,\rho}$ – stoichiometric coefficient of the component number *j* in the specific chemical reaction *r* number *ρ*; *R* – molar reflux ratio; *f* – ratio of vapor and liquid streams.

Heat balance:

$$\frac{R}{R+1}\cdot\left(\frac{1}{R}+\frac{1}{R}\cdot\left(\frac{1}{R+1}+\left(\frac{1}{R+1}\right)^{i}+\left(\frac{R}{R+1}\right)^{i}+\frac{r_d}{H_d}\cdot\left(\frac{R}{R+1}\right)^{i}+\ldots+\frac{r_d}{H_d}\cdot\left(\frac{R}{R+1}\right)^{i}-\frac{r_d}{H_d}\cdot\left(\frac{R}{R+1}\right)^{i}+\frac{r_i}{H_d}-\frac{r_d}{H_d}\right)+\frac{r_d}{H_d}\right)+$$
$$+\frac{\Delta H_{ch.r.}}{H_d}\cdot\frac{U_i}{L_i}\cdot\sum_{\rho=1}^{m}v_{j,\rho}\cdot r_{i,\rho}-\frac{H_{G_{i+1}}}{H_d}=F_2^h(R). \quad (3)$$

$H_{G_{i+1}}$ - enthalpy of vapor on the *i*+1 stage, kJ/kgmole; r_d – specific evaporation heat of the distillate, kJ/kgmole; r_i – specific evaporation heat of liquid on the stage number *i*, kJ/kgmole.

For steady state multiplicity analysis it is necessary to reveal potential nonlinearity sources. As provided by the mathematical model, nonlinear member of the model is reflux ratio. Every solution of the equations (2), (3) with physical meanings of R which satisfy the following conditions

$$F_2^m(R)=0, F_2^h(R)=0\,, \quad (21)$$

corresponds to steady state [3].

The result of the calculation for the reactive section is presented in table 1.

Table 1. Reflux (R) ratio, corresponding to steady states multiplicity region

№ of tray	3	4	5	6	7	8	9	10 (feed tray)
R	2.36	-	0.42	1.46	2.49	3.47	4.48	-

Table 1 shows that the reflux ratios, corresponding to one steady state, should meet the following requirements: *R*≥4.48.

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V-40

LACTIDE POLYMERIZATION REACTOR

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Currently polylactic acid (PLA) is one of the most promising biodegradable polymers due to the unique set of its valuable performance properties. PLA is manufactured from lactic acid obtained by microbial fermentation of carbohydrate waste. It is obtained by the following route: lactic acid → oligolactate → cyclic dimer (lactide) → polylactide.

PLA manufacturing is based on a polymerisation with ring-opening. The most common catalyst is tin 2-ethylhexanoate. Polymerisation is initiated by hydroxyl-containing compounds. The role of tin compounds was studied by several authors. There are sufficient data available describing real-world process in the synthesis reactor. For the building of the simulation model a few more data is required. It would allow us to build a proper simulation, study different work regimes and avoid unnecessary intermediate upscaling.

It was shown in [1] that impurities present in the monomer could determine the molecular mass and inhibit the polymerisation. Thus, in presence of water or alcohols the molecular mass is decreased but the reaction rate is not changed significantly. On the opposite, acid impurities, such as lactic acid or other acid species lower the polymerisation rate but do not influence significantly the resulting molecular mass. Lactide polymerisation is an equilibrium process and higher reaction temperature leads to both higher equilibrium monomer concentration and greater possible molecular mass.

In this work we studied lactide polymerisation catalysed by tin (II) compounds in 130 – 180 °C temperature range and at catalyst concentrations 0.1 – 0.01% mass in a batch reactor equipped with an anchor stirrer, reflux, nitrogen inlet, and a temperature control unit. During the process the monomer conversion degree and product molecular mass were monitored. For the simulation model we used kinetic data [2] and data on heat transfer coefficients and viscosity of the reaction mixture [3].

The simulation of the process allowed us to design the heater, determine residence times and lactide concentration in the melt. The real experiments were run on a pilot plant and optimal operational parameters were determined.

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PREPARATION OF DL-LACTIDE FROM MICROBIAL LACTIC ACID

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The current developments in medicine and pharma demand new polymeric materials for implants, filaments and controlled release systems. The significant share of these materials is manufactured from DL-lactide-glycolide copolymer. The synthesis of DL-lactide from readily available microbial lactic acid looks fairly promising. The irony is that all current efforts are directed to the microbial synthesis of L-lactic acid. Nevertheless, a significant amount of meso-lactide is formed as well. Usually it increases the process costs as the recycle of the meso-isomer is impossible. Thus, the insertion of a racemisation step into a classical route below

lactic acid → oligolactate → cyclic dimer (lactide) → polylactide

allows to obtain a racemate together with the L-isomer.

Generally, there are tow methods: racemisation of the starting oligomer and lactide racemisation [1]. Inversion of configuration starts at temperatures above 210 °C. The reaction rate is not influenced by the catalyst concentration and is determined by the temperature only.

In this work we studied thermal racemisation of oligolactide at 250 – 300 °C under nitrogen blanket. The following parameters were monitored: specific rotation, oligomer molecular mass, composition of low molecular weight by-products, content of cross-linking products. Upon thermal treatment oligomer was depolymerised to form the lactide. The experimental set up comprised a 5 litre glass-lined stirred reactor with an attached tube reactor. The flow chart is shown on the drawing. Reaction products were analysed by HPLC and GC-MS.

The temperature profiles of oligomer molecular mass and composition of low molecular weight by-products were obtained. Racemisation rate constants were also determined. We estimated the factors influencing meso-L – DL-lactide ratio in depolymerisation products. The reaction conditions were optimised for the maximum yield of DL-lactide.

The opportunity to transform reaction by-products into a significant amount of DL-lactide by oligomerisation with subsequent depolymerisation is a significant breakthrough.

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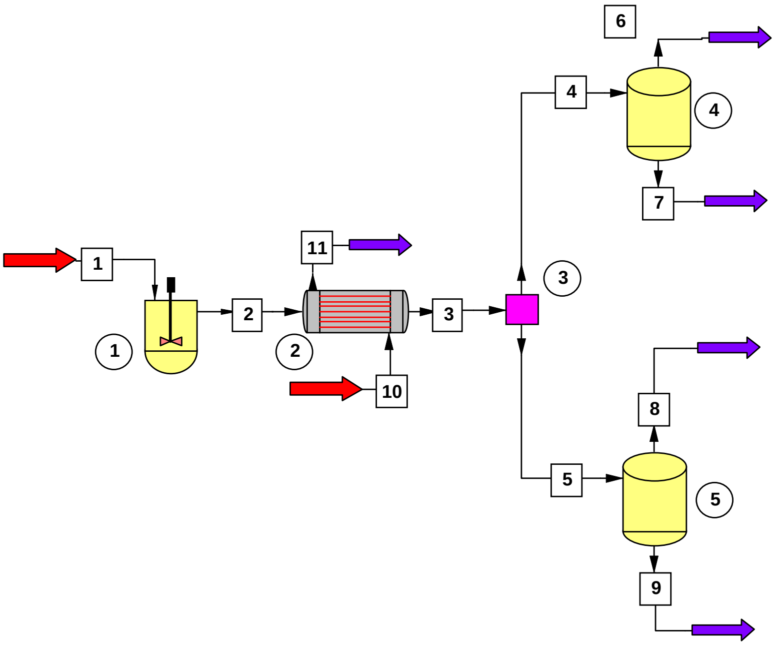

Flowchart of the depolymerisation plant:
1,2 – depolymerisation reactors; 3 – stream divider; 4,5 – tanks.

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V-42

PROCESS DYNAMICS IN SLURRY POLYMERIZATION

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The testing procedure of olefins polymerization catalysts has been examined. The reaction rate dynamics was studied and contributions of feed flow, gas - liquid mass transfer, polymerization reaction and catalyst deactivation were estimated. It has been shown, that the reaction rate during first 20-30 minutes is much lower (3 to 7 times) than total monomer consumption.

A polymerization catalyst testing is usually carried out in semi-batch reactor. The rate of monomer absorption by catalytic suspension is usually considered as a rate of reaction. In fact, the maximal consumption of monomer corresponds to its dissolution in solvent, but not to the rate of polymerization.

In this work we have measured the rate of gas-liquid mass transfer in an independent experiment using propylene dissolution into heptane (Fig. 1). The total propylene flow (W) is calculated by equation follows from Hagen-Poiseuille law:

$$W=\frac{k_h}{\sqrt{P_z}}\sqrt{P_z-P}\;\varphi(t)\,,\qquad \varphi(t)=\alpha\left(1-exp(-t/t_R)\right) \tag{1}$$

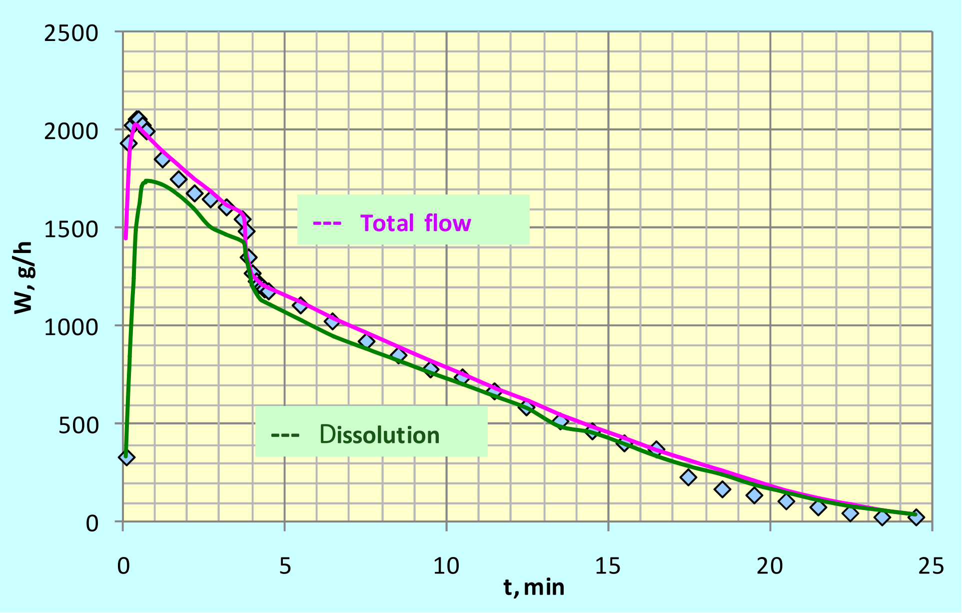

Fig. 1. Propylene dissolution in heptane at T = 70 °C and P = 10 bar.
Points – experimental flow; Lines – calculation by model (1-2).

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Propylene partial pressure in a gas phase ($P_m = P\,y_m$) and its concentration in liquid phase (C_m) depend on gas–liquid mass transfer and equilibrium:

$$\frac{dP_m}{dt} = W\frac{RT}{MV_G} - \beta\left(C_m^* - C_m\right)RT\frac{V_L}{V_G}\,, \qquad \frac{dC_m}{dt} = \beta\left(C_m^* - C_m\right) \tag{2}$$

In the presence of Ziegler-Natta catalyst, the reaction rate (R_p) and catalyst deactivation rate (da/dt) change the dynamics of propylene consumption:

$$\frac{dC_m}{dt} = \beta\left(C_m^* - C_m\right) - R_P\,, \qquad \psi = \frac{b_A C_A + b_H C_H}{\left(1 + b_A C_A + b_H C_H\right)^2} \tag{3}$$

$$R_P = k_P G_c C_m \psi a\,, \qquad \frac{da}{dt} = k_a C_A C_m a_i^o \exp\left(-k_a C_A t\right) - k_d a + k_s(1-a) \tag{4}$$

where k_h – constant (depends on apparatus); P, P_z – current and desirable pressure;

$\varphi(t)$ – transient response function; t_R – time constant of regulator; M – molecular weight;

V_L, V_G – volume of liquid and gas; β – mass transfer coefficient; a – relative activity;

C^*_m – equilibrium concentration; k_P – reaction rate constant; G_C – weight of catalyst;

C_A, C_H – Al(Et)$_3$ and H$_2$ concentration in liquid; b_A, b_H – their adsorption coefficients;

k_a, k_d, k_s – rate constants of active centers activation, deactivation, and self-regeneration.

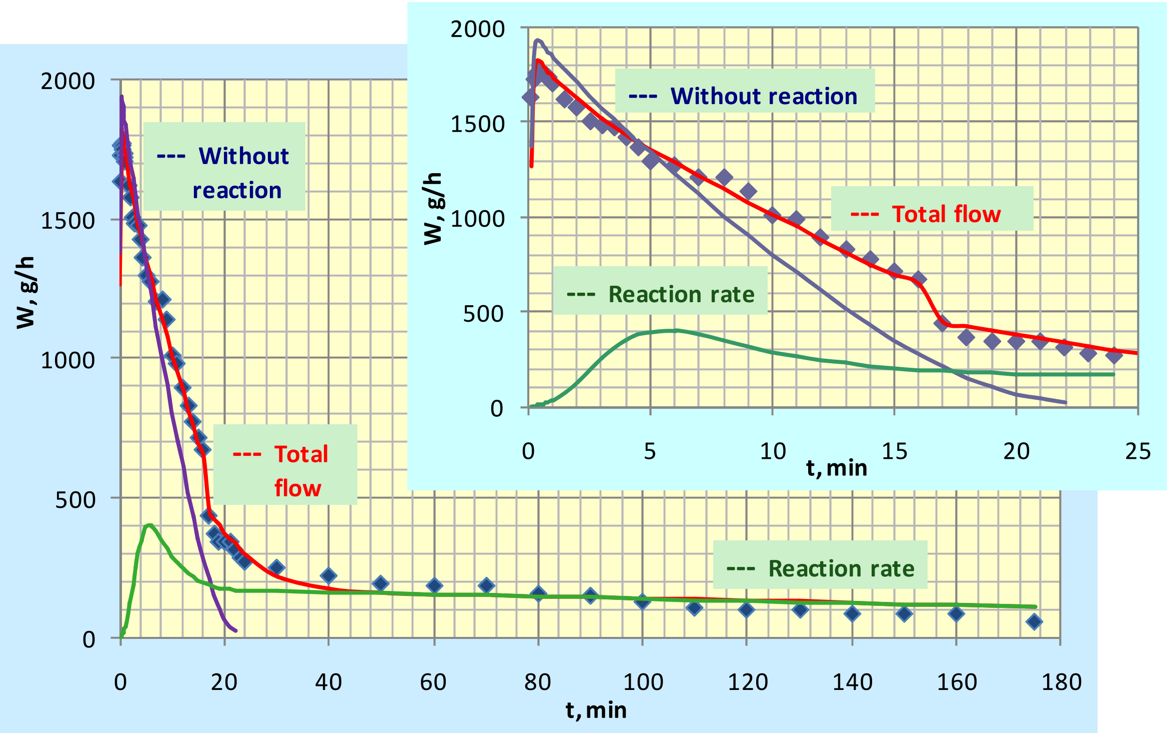

Fig. 2. Propylene flow dynamics during polymerization at T = 70 °C and P = 10 bar.
Points – experimental flow; Lines – calculation by model (1–4).

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EQUILIBRIUM LIMITED REACTIONS: A CASE STUDY OF KINETIC PARAMETERS EVALUATION FOR ETHYLENE-GLYCOL ESTERIFICATION

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The resulting products of monoesterifications of diols are of considerable practical interest, because they are widely used for cosmetical, pharmaceutical and nutritional purposes. This kind of reactions are reversible and can be conducted with various acids [1-3]. The aim of the present study was to determine the kinetic parameters of ethylene glycol monoesterification. The reaction was performed using benzoic acid in the mixture of Al_2O_3 and methanesulphonic acid.

All the experiments were carried out in an automated laboratory batch reactor. The reactor was equipped with the FTIR based ReactIR^{TM} iC10 analysis system used for the real time monitoring of 2-hydroxyethyl benzoate concentration profiles. As an example the FTIR spectra collected during one selected experiment is presented in Fig. 1. It can be clearly seen that the intensity of the peak (absorbance, A) within the wavenumber range, ν = (1440–1470) cm^{-1} increases over the reaction time. After a certain period of time, depending on experimental conditions, equilibrium steady state is formed.

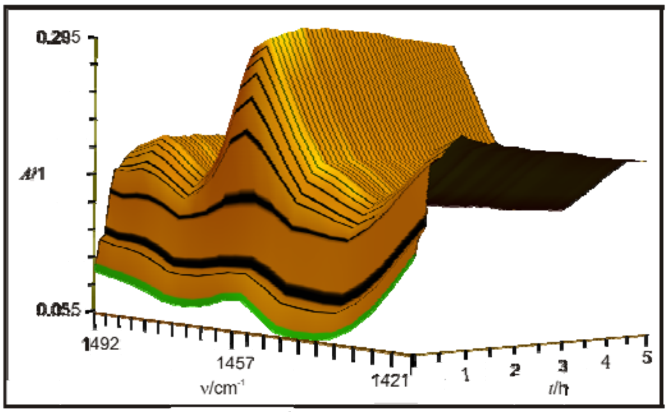

Figure 1: Waterfall plots of FTIR spectra during the monoesterification of ethylene glycol at temperature, ϑ = 70 °C.

The FTIR spectra were transformed to the real-time concentration profiles of 2-hydroxyethyl benzoate considering peak areas treatment of the corresponding peak with two point base line correction. The concentration of the product in the reaction mixture was determined using calibration curve. For that purpose 2-hydroxyethyl benzoate was synthesized and further cleaned, because this compound was not available as a standard at the market.

After analytic integration of the rate expression for second-order reversible reaction the performance equation was developed. By plotting the term ln(X_{Ae}-(2X_{Ae}-1)X_A)/(X_{Ae}-X_A) versus time it was possible to calculate the reaction rate constant, k_1. Another constant, k_2, for the reverse reaction was obtained from the equilibrium constant. Experiments at five different temperatures were studied. From the Arrhenius plot (Fig. 2) we determined the activation energy, E_{a1} = (100.4 ± 1.8) kJ mol^{-1} and the pre-exponential factor, k_{01} = (3.6 ± 3.1) 10^{12} L mol^{-1} min^{-1} for the forward reaction. For the reverse reaction we obtained the values for E_{a2} = (118.3 ± 1.8) kJ mol^{-1} and k_{02} = (1.1 ± 1.0) 10^{14} L mol^{-1} min^{-1}, respectively.

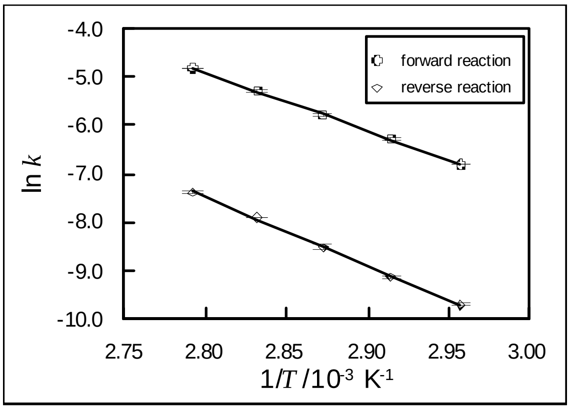

Figure 2: Experimental and Arrhenius model-based values of the logarithm of reaction rate constants, ln k_1 and ln k_2, in relation to 1/T.

The literature contains numerous reports on kinetic models of consecutive chemical reactions. However, much less attention has been paid to the design for the equally prevalent class of reversible reactions. The results of this study could be applied to the control of investigated chemical reaction at the molecular level, which strongly depends on kinetics and mechanism.

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PIROGAZIFICATION PULVERIZED OIL SHALE IN FLOWING TUBULAR REACTOR

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To be able to control termodestruktivnymi processes of organic matter decomposition of solid fuels in their pirogazification is proposed to carry out reprocessing in flow tube reactors, located in a high-boiling layer. Particulate transported shale gas flow in the reactor and getting through the wall of the reactor heat from the fluidized bed, heated to a final temperature of the process. Fluidized bed is formed chemically inert solid particles, which are fluidized combustion of coke residues resulting from pirogazification shale. Active expansion of the oil shale kerogen particles $d_T = 110 \div 220$ of micron size in air at a heating rate of $dt_T / d\tau \cong 10^3$ °C/s begins with a temperature of 250÷200 °C.

Processing of experimental data on the thermal-oxidative pyrolysis in air powdered sulfur Volga shale deposits Kashira (in dry weight – 58,25% ash, 13,29% of carbonates, kerogen 28,47%) at temperatures in the range of the process t_Π = 600÷750 °C led to the following correlation relations:

- for the reaction rate

$$\frac{dc}{d\tau} = 0{,}81 \cdot 10^{15} c^{-0{,}78} \, exp\left[-\left(1554560 - 2738T + 1{,}47T^2\right)/\left(R_M T\right)\right]; \qquad (1)$$

- for the heat liberated in the reactions

$$q_P = 1634 g_B^{0{,}968}\text{, KJ/kg suh.sl.}; \qquad (2)$$

- for the supplied heat through the wall of the reactor (including heat balance of the reactor)

$$\tilde{q} = 1{,}65 g_\Gamma t_\Pi + 1{,}3 g_K t_\Pi - 1{,}1 t_{T,0} - g_B t_{\Gamma,O} - q_P\text{, KJ/kg suh.sl.}, \qquad (3)$$

where $c = (g_\Gamma - g_B)/g_{OP\Gamma}$ – the conditional concentration of this gas; τ – time, sec; T – the absolute temperature of the process, K; R_M = 8,314 J/(mol · K) - the universal gas constant; g_Γ – yield of pyrolysis gas, kg/kg suh.sl.; g_K – the output of coke, kg/kg suh.sl.; $g_{OP\Gamma}$ – content of kerogen in the shale source, kg/kg suh.sl.; g_B – specific air flow rate, kg/kg suh.sl.;

$t_{П}$ – the final temperature of pyrolysis, °C; $t_{Т,0}$ and $t_{Г,0}$ – initial temperature of oil shale and air, °C.

Calculations performed using the above given formula known from the literature data on heat transfer fluid layer placed in the furnace tubes and our data on heat transfer fuel gas suspension to the wall of the reactor, shown, in particular, the following.

Quantity of coke produced from oil shale during pyrolysis of $g_{К} \cong 0,75 \div 0,85$ kg/kg suh.sl. The demand for coke in the furnace to supply the installation considerably smaller, amounting to $g_{К,ТОП} = 0,184$ kg/kg suh.sl. at $t_{П} = 600$ °C, and 0,208 kg/kg suh.sl. at 700 °C. Consequently, the pyrolysis of oil shale on the thermal energy is independent of external sources.

For particle size fluidized bed $d_{Т,К.СЛ} = 6$ mm may include space arrangement. In the fluidized bed height of 1.8 meters and an area of the gas distribution grid 5,3 × 1 m placed in increments of $S_1 = 3D$ and $S_2 = 0,866 S_1$ reactors with a diameter $D = 0,02$ m. Number of reactors $N = 630$, their total surface area of heat transfer $F_{\Sigma} = 212$ m^2. At a flow rate of oil shale in a reactor, $G_{Т,0} = 0,02$ kg/s, the performance of the processed fuel plant for over 46 t/h or 1104 t/day. The development of pyrolysis gas at $V_{В} = 100$ l / kg suh.sl. and $t_{П} = 600$ °C will be $G_{Г} = 400$ tons/day and coke (net supply to the furnace) $G_{К} = 618$ tons/day. Transmitted by a fluidized bed heat capacity is 5 MW and the total heat capacity, taking into account the thermal effect of the pyrolysis reactions - 8 MW.

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ISOPROPILBENZENE REACTOR MODELING

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Isopropilbenzene (IPB) production on the sulphocationite catalyst Amberlyst-36 makes possible to carry out benzene alkylation with propylene (in propane-propylene mixture PPF) in the isothermal mode (temperature 80 degrees C.).

$$C_6H_6 + CH_2 = CH_2 - CH_3 \rightarrow C_6H_5 - CH(CH_3)_2$$

Side reactions cause some products of the sequential addition, diisopropylbenzene (DIPB) and polialkilbenzenes (PAB), which cause resin formation on the catalyst.

In the article [1] a kinetic equation of the first order has been supposed

$$r = \frac{k \cdot [H^+]^n \cdot \alpha_A \cdot \alpha_B \cdot \beta_A \cdot \beta_B}{\left(\sum_j \alpha_i \cdot \beta_i\right)^2} \cdot \left(1 - \frac{\alpha_C}{K_a \cdot \alpha_A \cdot \alpha_B} \cdot \frac{\sum_j \alpha_j \cdot \beta_j}{\sum_j \alpha_j^p \cdot \beta_j}\right)$$

to describe the dates [2] in the batch operated reactor of mixing (table 1).

Table 1

Hydrocarbons, conversion, selectivity.	Concentration, % mass./ hs				
	Start	0,5	1,0	2,0	4,0
Propane	2,6	2,6	2,6	2,6	2,6
Propylen	10,3	4,6	2,7	0,7	0,06
Benzene	87,1	76,2	73,0	69,3	68,1
Isopropylbenzene	-	15,6	20,5	25,3	26,2
DIPB	-	0,6	0,98	1,83	2,63
PAB	-	-	0,02	0,03	0,05

The alkylation reactor is a cascade of four reactors made like a common apparatus with flows intermediate cooling inside built-in tubular heat exchangers.

PPF is fed into the each reactor discretely. It allows holding necessary molar ratio propylene: benzene.

The mathematical model of the benzene alkylation process with propylene has been found expedient to run with Unisim Design program, because given specialized packet has got basically a wide base of the physical chemical constants of the individual chemical substances, thermodynamical equations set and status equations.

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To create ideal mixing reactor model (fig. 1) alkylation reactions equations have been defined; Peng-Robinson thermodynamic packet has been chosen; reaction type has been selected (heterogeneous catalytic one); stoichiometric coefficients have been arranged. Under simulation conditions the material and energy flows have been specified and the reactor volume has been given either.

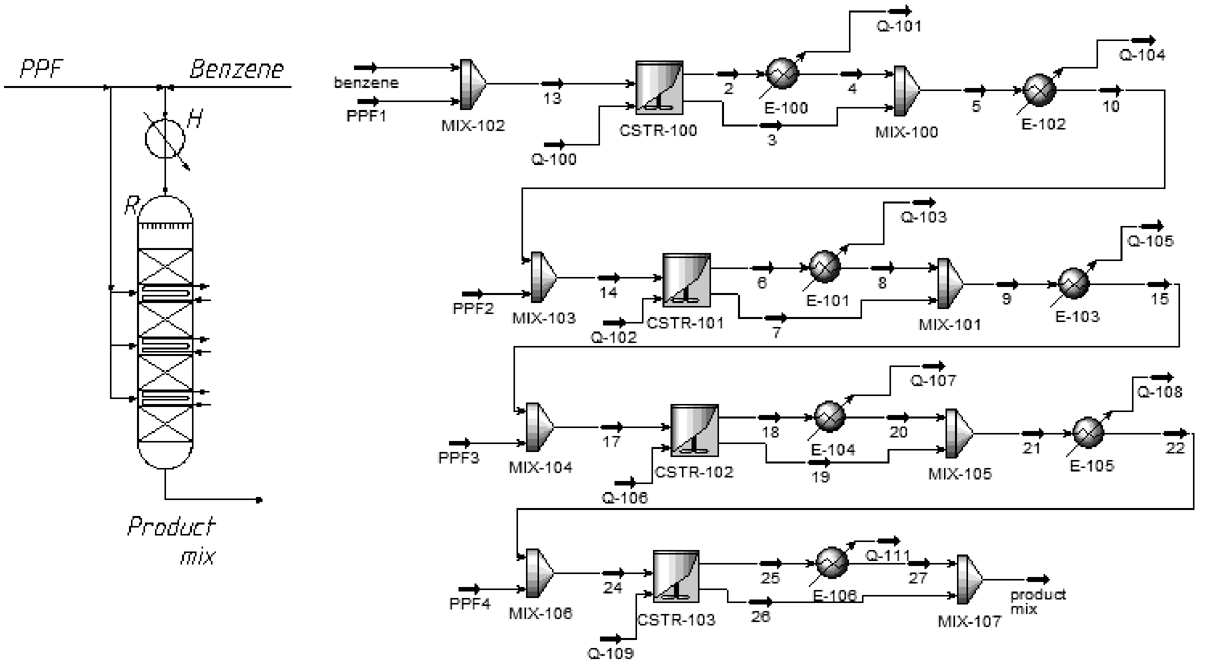

Fig. 1. Reactor model.

Relying on the data for input and output concentrations of the components (table 1), the kinetic inverse problem has been solved.

For the obtained model it is possible to carry out computer experiments with ratios varying both for the main reagents and under PPF conditions. The ratios depend on the process selectivity.

Obtained results examination allows determining the optimal terms for isopropylbenzene production using benzene alkylation with propylene.

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OSCILLATIONS AND BIFURCATIONS ON THE REACTOR OF FULL MIXING IN FLOW (RFMF)

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It is known that reactors of full mixing in flow are convenient tools for the investigation of dynamic regimes at the oxidation of complex compounds (organic compounds).

However, frequently researchers manage to register only one mode of regime and it is not always possible to register experimentally the bifurcation change of a dynamic mode (to fix the moment of bifurcation).

In given work there are presented the results of experimental investigation of dynamic modes occurring in flow reactor of full mixing, under low temperature oxidation of propane depending on organization of process and treatment of surface of the reaction vessel.

The theoretical model has been developed which explains the observed phenomena, namely inhibitors of reaction formatted on the surface of reaction vessel and penetrating the volume, resulting to bifurcation change in reaction medium and causing oscillation in reactor. In fig. 1. it is presented general schematic creation of experimental devices.

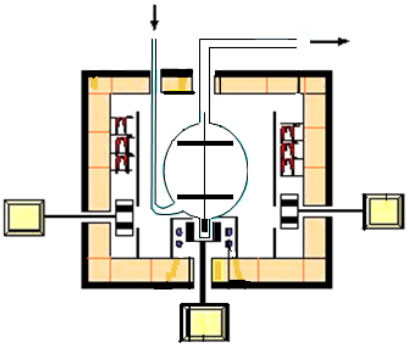

Fig. 1. The reactor and furnace schema.

In fig. 2 it is shown an experimental result of a carried out reaction of oxidation of propane. At first the mix of air with propane is kept in a reactor without a stream about five minutes, then the reactor is pumping up to 2 - 3 Torr. After, reactor is filled with air again, and after the beginning of submission of air, after approximately 4-5 seconds submission of propane is conducted. It is apparent, that submission of air strengthens the reaction, and after submission of propane reaction strongly amplifies (Curve. 1.). However, after the beginning of submission of propane, after approximately 2 seconds in a reactor bifurcation occurs (which is related to penetration of products of heterogeneous recombination in volume by inhibiting the process), and reaction continues to amplify much more slowly on a curve 2, and simultaneously in system pulsations take place.

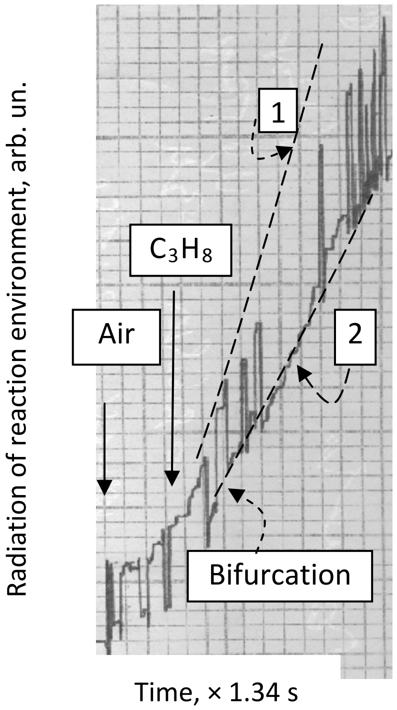

Fig. 2. Pulsations in a RFMF at oxidation of propane in air.
Curve. 1. (Dotted line) - continuation of a course of reaction if bifurcation has not taken place;
Curve. 2. (Dotted line) - a course of an intensification after bifurcation in system.

The submission of air to the environment of intermediate poorly linked products of reaction strengthens the reaction, and the submission of propane intensifies the reaction even more strongly.

Also it is visible; that in system bifurcation occurs then the mode of reaction varies from steady growth on oscillating.

It is offered the model of oxidation of organic connections explaining this phenomenon.

Theoretical consideration of this question in that specific case, namely, in case of a birth of excited inhibitor of reactions at heterogeneous recombination and its hits in volume is suggested by us in case of low temperature oxidations of organic connections. The model includes the basic homogeneous-heterogeneous stages, playing fundamental role at low temperature oxidations of organic connections: $Z + A \rightarrow X + C$ k_1; (2) $X + B \rightarrow Z + L$ k_2; (3) $L + S \rightarrow X'S + Y$ k_3; (4) $Y + B \rightarrow Z + D$ k_4; (5) $X + S \rightarrow XS$ k_5; (6) $XS + X'S \rightarrow In^* + 2S$ k_6; 7) $In^* + X \rightarrow$ Prod. k_7; (8) $In^* \rightarrow$ Stab. k_8.

Where A, B – initial compounds; X, Y, Z – active particles; S – surface active centre; XS, X'S – adsorbed on the surface active particles; L – low stable intermediate product; C, D – products; In* – excited inhibitor. This model brings to pulsations in system in a wide range of values of parameters.

DESIGN OF REACTORS WITH STRUCTURED PACKED FOR HYDROGENATION OF HYDROXYCARBOXYLIC ACID ESTERS

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Production of valuable chemical substances out of renewable natural products has been attracting much attention recently. One of the prospective processes for obtaining propylene glycol is selective catalytic hydrogenation of lactic acid. Nevertheless, most known catalysts require rather hard process conditions. On the other hand, it is well known that carboxylic acids esters are more active in reactions for obtaining alcohols as compared to free acids. Currently used sintered and deposited commercial metal catalysts have relatively low activity in lactic acid esters hydrogenation. Conversion and selectivity of the process can be increased by using structured catalytic layers, which start to play important role in industrial chemical processes. High surface area of the catalyst packing provides intensive heat- and mass-transfer rates and effective fluid mixing. Investigation of the block reactors and structured catalytic packing systems leads to the conclusion that they can be effectively used for lactic acid esters hydrogenation process.

Figure 1 shows the scheme of structured catalyst packing reactor for hydrogenation. Hydrogenation reactor consists of a stainless steel tube (20mm in diameter), bottom part of which is equipped with a supporting grid. Reactor is filled with a catalyst packing; active phase surface coverage degree may vary depending on the packing orientation. Catalyst-less packing for mixing and heating the reagents is situated in the upper part of the reactor. There is also some catalyst-less

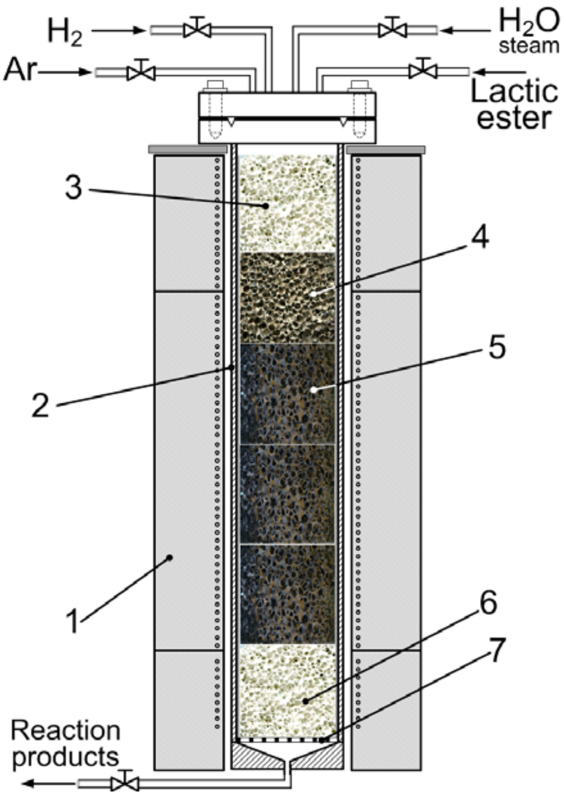

Fig. 1. Experimental set up.
1 – three zone furnace; 2 – reactor; 3, 6 – catalyst-less packing; 4 – precatalyst packing; 5 - catalyst packing; 7 – grid.

packing in the bottom part of the reactor which serves the purpose of cooling and separation of reaction mixture. The amount of catalyst deposited on the packing varies depending on the required height-temperature profile. In this research, reactor temperature varied from 120°C up to 230°C (pressure was in the interval 0.1-1.2 MPa).

Structured catalyst packing consists of either foamed alumina (corundum) (figure 2) or catalyst deposited on pre-formed by catalytic chemical vapor deposition layer of multi-walled carbon nanotubes (figure 3).

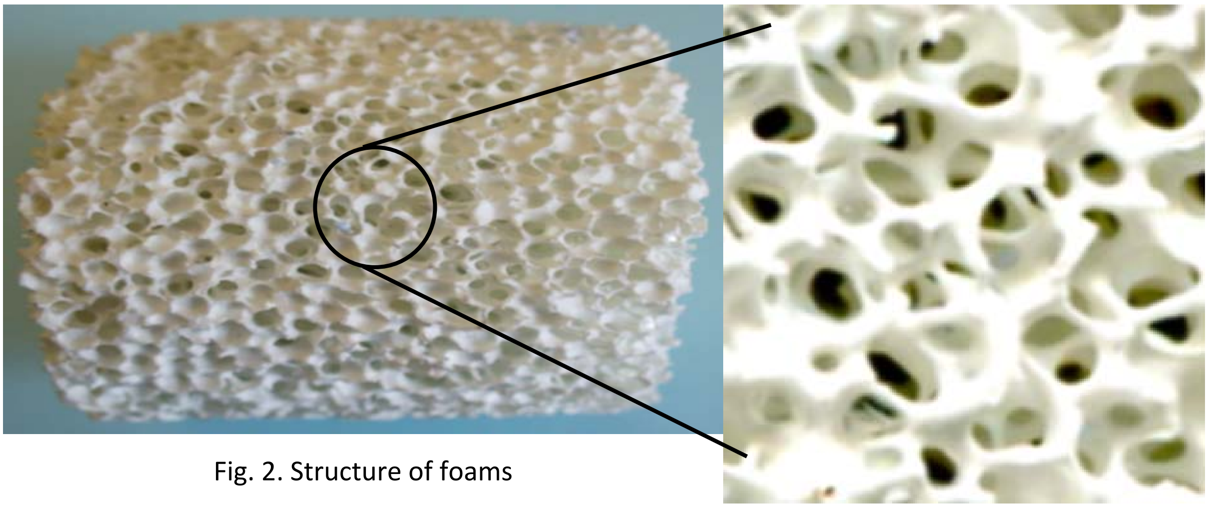

Fig. 2. Structure of foams

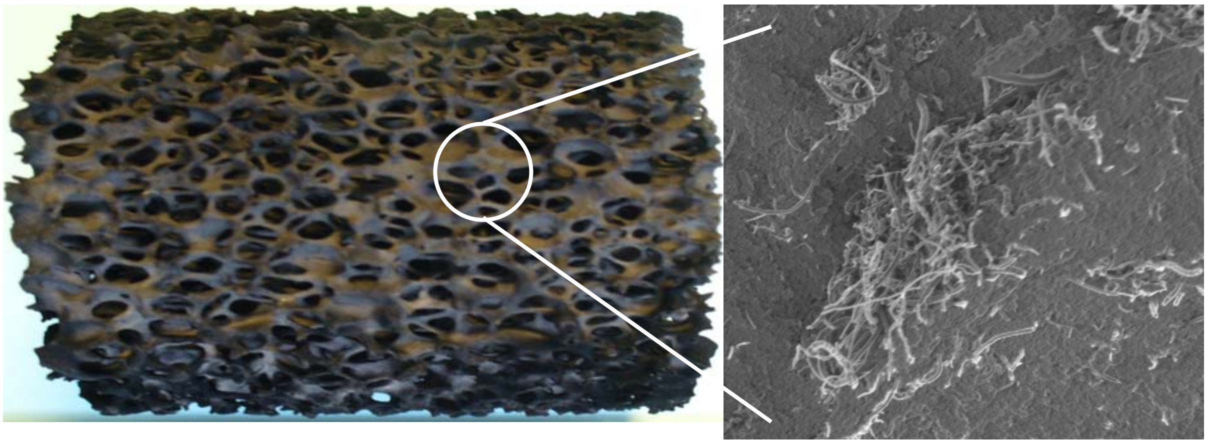

Fig. 3. Structure of foams with MWN

SEM-image of foams with MWN

Effect of residence time on methyl- and butyl-lactate conversion degree and propylene glycol formation selectivity was investigated. Experiments were carried out at different temperatures and reaction mixture bulk speeds while keeping the hydrogen to ester mole ratio constant. Based on this data, effective rate constants and activation energies for 1-hyroxy-2-propanone and propylene glycol formation reactions were computed. Conversion degree for methyl-lactate was found to be 71%, for butyl-lactate – 76%, propylene glycol formation selectivity 92-95%.

OPTIMIZATION OF TECHNOLOGICAL PROCESSES OF SYNTHESIS OF MONOMERS FOR BIODEGRADABLE POLYMERS BASED ON MEMBRANE BIOREACTOR

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Currently, lactic acid and its derivatives are attracting interest due to availability of feedstock and its low cost. Many researchers are engaged in R&D in this field.

The disadvantage of the conventional batch-wise fermentation is its low productivity. The lactic acid could be produced simply and inexpensively under conditions where the rate of cell growth is just sufficient for the replacement of dead cells, thus decreasing the consumption of carbohydrates per unit of lactate.

The pilot plant for obtaining microbial lactic acid was built at the Krasnodar Branch of the Federal State Enterprise 'Plant Bio Protection Agents'. Using membrane bioreactor with recycle it was possible to get cell concentration as high as 100 g/L (dried cell weight) and even more. By optimising process parameters it is possible to obtain a volumetric productivity exceeding 100 g/L/h. A mathematical model of the membrane bio-reactor was developed and used to optimise the process conditions.

Lactic acid is the feedstock for obtaining lactate, lactide and the biodegradable polymers [1]:

Starch → Ammonium lactate → Calcium lactate → Lactate ester → Oligomer → L- and DL-lactide → (co)polylactide

The second stage is an esterification of calcium lactate to produce lactate ester and recover calcium chloride, which is use in the first stage to precipitate lactate. No calcium sulphate waste is formed as opposite to the conventional lactic acid isolation. Lactates obtained at this stage are used as the raw material for the synthesis of oligomers and may themselves be commercial products.

Lactide was produced from oligomer at the fifth step. The thermodestruction of oligolactic acid was studied on the pilot plant [2]. The process was described by the system of differential rate equations. The model satisfactorily simulates the pyrolysis of oligolactic acid and rate constants were determined. It was shown that for manufacturing a high purity product higher molecular weight feedstock should be used. That results in longer process times. The main impurities are low molecular weight homologues with polymerisation degree 1–3. No significant changes in a molecular mass and molecular mass distribution occur during the pyrolysis. The only changes that have place occur at the initial steps and are due to stripping of light components and, possibly, depolymerisation. When the oligomer molecular mass Mn reaches a certain threshold value no further changes occur. Pilot plant trials showed the good agreement of simulation and experiment.

Generally, there are two methods: racemisation of the starting oligomer and lactide racemisation [3]. Inversion of configuration starts at temperatures above 210 °C. The reaction rate is not influenced by the catalyst concentration and is determined by the temperature only.

The thermal racemisation of oligolactide was studied at 250 – 300 °C under nitrogen blanket. Upon thermal treatment oligomer was depolymerised to form the lactide. The experimental set up comprised a 5 litre glass-lined stirred reactor with an attached tube reactor.

The temperature profiles of oligomer molecular mass and composition of low molecular weight by-products were obtained. Racemisation rate constants were also determined. We estimated the factors influencing meso-L – DL-lactide ratio in depolymerisation products. The reaction conditions were optimised for the maximum yield of DL-lactide. The opportunity to transform reaction by-products into a significant amount of DL-lactide by oligomerisation with subsequent depolymerisation is a significant breakthrough.

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PERFORMANCE OF ONE-DIMENSIONAL APPROXIMATIONS TO PREDICT EFFECTIVENESS FACTOR FOR PELLETS WITH ARBITRARY SHAPE AND ABNORMAL KINETICS

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Intra-particle diffusion limitations most often has to be properly taken into account to obtain reliable results when modeling catalytic fixed beds. In general, mass balances inside a real pellet should be stated for two (2D) or three (3D) spatial coordinates and a numerical solution is to be undertaken. This computational task is affordable for a single set of conditions, but it is clear that even for the simplest practical case (e.g. simulation of a catalytic reactor with a single reaction) the calculations have to be performed thousands of times. Problems like reactor optimization further increase the amount of numerical calculations. Then, it is highly convenient or even necessary to avoid the use of 2D or 3D computations.

Aris [1] presented a very simple approach to reduce 2D or 3D problems into a 1D problem showing that at large values of the Thiele modulus (Φ), the effectiveness factor (η) for a single reaction does not depend on the pellet shape, but just on the characteristic length ℓ (i.e, the ratio between pellet volume and external surface area). Approximate evaluations for any Φ can be carried out adopting a simple geometry that satisfies the actual value of ℓ. The expected precision is about 20% for relatively simple kinetics.

Datta and Leung [2] proposed a more suitable 1D model, called generalized cylinder (1D-GC), assuming that diffusion takes place along a distance L of a hypothetical body of variable cross section according to z^{σ}, being z the non-dimensional coordinate. Values of the two model parameters, L (effective diffusion length) and σ (shape factor), can be obtained by matching the value of ℓ and one additional property linked with the shape of the actual pellet.

Mariani et al. [3, 4] proposed two criteria to estimate σ by stating that the 1D-GC model response should exactly match the values of the actual pellet either at high or low effective reaction rates, respectively. The expected errors of the 1D-GC model using the high reaction rate criteria are less than 3% for a variety of pellets with normal kinetic behavior (i.e. η

decreases monotonically as Φ increases). Nonetheless, the use of 1D-GC model for some shapes of commercial pellets can lead to considerably larger errors than the above mentioned level when some of the ratios between geometrical dimensions of the pellet reach some critical values, even for isothermal linear kinetics. Therefore, to restore the precision it was necessary to propose a novel one-dimensional model, termed variable-diffusivity model (1D-VD), which introduces three parameters evaluated by satisfying simultaneously the behavior of the actual pellet at high and low reaction rates. It was checked that the 1D-VD model warranties a precision better than 2% for isothermal lineal kinetics and a vast set of particles with critical geometrical dimensions [5].

In this context, the aim of this contribution is to thoroughly test the effect of kinetic expressions on the prediction of effectiveness factor by one-dimensional models, extending the analysis up to near the limit of steady state multiplicity for a representative set of pellet shapes. Different types of abnormal kinetic expressions (presenting a maximum of the reaction rate with the concentration of the key species) including thermal and self-inhibition effects were tested. Also the limiting reactant order and reversibility effects were analyzed. η for the actual geometry of the pellets was numerically obtained using the Comsol Multiphysics platform. These values were compared with the predictions from 1D-VD and GC-1D models for every particle and kinetic expression for the whole range of Φ. In all the cases the pellet height was varied from 0 to ∞ to detect challenging situations. For each kinetic expression, a kinetic parameter can be identified as leading to steady state multiplicity. For values of such parameter less than 90% of the critical value that introduce multiplicity, the 1D-VD model is able to predict effectiveness factor with maximum errors of around 10% for the whole range of Thiele modulus. At the same conditions, the 1D-GC model show errors of up to 40%. In summary, it is shown that the 1D-VD is a suitable approximation to estimate η even for abnormal kinetics near the limit steady state multiplicity.

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AUTOCLAVE HYDROGENATION OF BIOETHANOL CONVERSION PRODUCTS

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Biomass is one of the promising alternative sources of energy and an important alternative raw source, as it's possible to produce bioethanol by its fermentation, and to produce further aromatic hydrocarbons, olefins and synthetic gasoline products.

In the course of this work zeolite-based catalysts were developed for the conversion of bioethanol into light olefins, aromatics, high-octane components for gasoline and diesel fuels. Catalytic process has conversion of almost 100% at 300-450°C and 1-6 atm. Under these conditions, lower olefins C2-C4 and a liquid fraction consisting mostly of C4-C9 hydrocarbons and of aromatics (toluene, xylene, ethylbenzene, other alkylated aromatics). Sum total of obtained aromatics can reach as high as 90% wt. Hydrogenation of this fraction allows to obtain the motor fuels (the percentage of aromatics falls down to 25%, and in the absence of benzene the resulting motor fuels have high quality). By varying the composition of a zeolite catalyst and the process conditions it is possible to increase the yield of heavy aromatics including that with the condensed nuclei in the liquid fraction with the purpose of naphtenes production (rocket fuel, etc.) by hydrogenation in an autoclave. Hydrogenation was conducted at 350°C and 100-120 atm. The resulting product was rich in naphtenes while the content of aromatics decreased to 21% wt.

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UNIVERSAL FLOW-TYPE REACTOR FOR CATALYTIC α-OLEFINS OLIGOMERIZATION

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The implementation of the α-olefin oligomerization reaction in a column flow-type reactor with a mechanical mixing device representing a multi-tier mixer with plane vanes has been discussed. The dependence of the mean residence time of the reaction mass in the apparatus on the space velocity of the flow has been experimentally found. It has been shown that the description of the oligomerization process in the said reactor by several logically acceptable kinetic models including those of: ideal reactor displacement, cascade of ideal mixing reactors, diffusional model, ideal displacement and ideal mixing reactors in succession, and visa verse, does not reveal any substantial difference in the final degree of α-olefin conversion to oligomers between the models under consideration. The reason of this may be attributed to the fact that in these computations the observed mean residence time, being a corrective factor while modeling is taken. For example, while using the ideal displacement reactor kinetic model on the kinetic parameters of decene-1 oligomerization at different temperatures a rather adequate approximation of the experimental and calculated values of the total olefin conversion to oligomers has been obtained. Given a sufficient experimental data base is available, the dependence of the yield, oligomer mean molecular mass and viscosity on the process conditions may by described by regressive equations and can be combined into a unified computer system permitting to control the oligomerization process in a flow-type reactor to produce oligomers with desired molecular-mass and viscosity characteristics. The reactor under discussion proves to be versatile for α-olefin oligomerization in the presence of pseudo-homogeneaus and homogeneaus catalyst. One of the definite advantages of the reactor consists in the combination of intensive reaction mass mixing being especially important while using pseudo-homogeneaus catalysts, providing for the required mean residence time to attain maximum possible monomer conversion.

PECULIARITIES OF ETHANE AROMATIZATION OVER Pt-CONTAINING ZEOLITE CATALYSTS

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The transition to production of chemicals from light hydrocarbons (ethane, propane, butane) has proven its effectiveness for the petrochemical industry in developed countries. On the other hand, the oil refinery products are still the main hydrocarbon feedstock for the chemical industry in Russia. To improve the competitiveness of Russian refineries and petrochemical plants, the problem of the use of light hydrocarbons have to be solved. Russia possesses substantial resources of ethane-containing gases suitable for processing at large gas chemical enterprises. One of possible applications of the ethane fraction is its conversion into liquid products over zeolite-containing catalysts [1, 2]. The practical implementation of this process allows increasing the production of aromatic compounds, and effective application of cheap raw gas stock. The aim of this work is to study the process of ethane conversion into aromatic hydrocarbons over the Pt-galloalumosilicate with the ZSM-5 structure.

The galloaluminosilicate (Ga-AS) with a silica ratio of 40 was obtained by the isomorphic substitution of Si(IV) atoms for Ga(III) in the zeolite crystal lattice during hydrothermal synthesis via partial substitution for aluminum ions by gallium ions in the precursor aluminosilica gel. The concentration of gallium oxide in the sample was 1.85 wt %. The galloaluminosilicate impregnated with the solution of platinum hydrochloric acid with the platinum concentration varying from 0.05 to 0.5 wt. % was dried at 110 °C and calcined in air at 550 °C for 5 h.

The conversion of ethane was carried out in a flow type installation equipped with a quartz reactor under atmospheric pressure, at the reaction temperature of 500-650 °C and a feed space velocity of 500 h^{-1}. The reaction products were analyzed by gas chromatography using the Crystal Chromatec 5000.2 chromatograph (Chromatec. Russia).

To assess the catalytic activity of the samples the degree of ethane conversion was determined and the selectivity towards formation of gaseous and liquid reaction products and their yield were calculated.

The main liquid products of ethane aromatization over Ga-AS are benzene, toluene, xylenes, and high molecular weight compounds, including naphthalene and its derivatives. The degree of ethane conversion and the yield of aromatic hydrocarbons increased to 43.5 and 27.3% respectively with increasing temperature to 650 °C. The selectivity towards formation of aromatic hydrocarbons within the temperature range 500-650 °C varies from 79.8 to 62.8%.

Due to the introduction of platinum into the galloalumosilicate, the activity of a catalyst was significantly increased, its selectivity towards the formation of aromatic hydrocarbons was enhanced, while the contribution of undesired reactions leading to the formation of co-products was reduced. The highest activity in the conversion of ethane and selectivity towards the formation of aromatic hydrocarbons was exhibited by the galloalumosilicate supplemented with 0.3% Pt. At 600 °C the ethane conversion and the yield of aromatic hydrocarbons in the 0.3% Pt/Ga-AS sample reached 63.1 and 43.6%, respectively, while the selectivity towards the formation of end product was 69.1%.

According to the TEM data due to the introduction of more than 0.1% of platinum into Ga-AS, the gallium migrates to the outer surface of the zeolite crystals, while platinum forms clusters in its channels no larger than 1 nm in size. In addition, the decrease in the gallium content in the inner space of the carrier channels with increasing platinum content was registered by the EDX-analysis. Apparently, in the course of ethane aromatization the composition of in-channel clusters changes towards their enrichment with the platinum atoms. The reduction of gallium ions results in the formation of amorphous spherical particles of metallic Ga with a mean diameter of about 13 nm on the surface of the carrier.

Thus, the galloalumosilicate supplemented with 0.3% Pt exhibits the highest activity and selectivity towards the formation of aromatic hydrocarbons from ethane, which is likely to be due to the increased concentration of platinum in its dispersed state and to the optimized composition and ratio between the catalytic centers of various origin.

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MATHEMATICAL MODELLING OF THE REACTOR OF METHANOL SYNTHESIS

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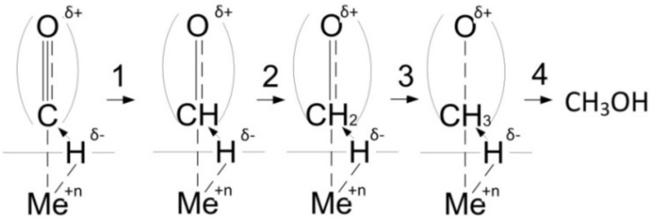
The methanol is the basic large-capacity products of the chemical industry. It is the basis of the major chemical compounds – organic chemicals, synthetic pitches and plastic, pesticides, pharmaceutical preparations and other compounds, that used as additives to increase the octane number of fuel [1]. The offer and demand of methanol has been increasing in the world from the beginning of 90th years till now [2].

The purpose of this work was creating the mathematical model of methanol synthesis on the low-temperature Zn-Cu-Al-catalyst and definition of effects from the possible variants of reconstruction of installation M-750.

The basis of the mathematical model is the superficial mechanism of synthesis, based on formation of positively charged complex lies. According to the given statement CO is adsorbed on a surface of the catalyst with formation of positively charged complex. Hydrogen under the influence of a high pressure and temperature cooperates with a catalyst surface and gets a negative charge. During interaction among adsorbed structures, there are a loosening between the active center of contact and the adsorbed molecule of CO, also interaction between absorbed complex and hydrogen, and detachment the formed molecule of a methanol from a surface of the catalyst [3]. The scheme of transformations of substances for the given mechanism of synthesis is resulted in drawing 1



Drawing 1. The superficial mechanism of synthesis of a methanol.

As kinetic model as the most suitable and full has been chosen the model resulted in work [4]. Values of speed of target reaction of synthesis of a methanol (1.1), conversion of CO (1.2) and synthesis of a methanol (1.3) for the given model have the following appearance:

V-53

$$r_1 = \frac{k_1 K_{CO} K_{H_2}^2 K_{CH_3CO} \left(P_{CO} P_{H_2}^2 - P_{CH_3OH} / K_{p1} \right)}{\left(1 + K_{CO} P_{CO} \right) \left(1 + K_{H_2}^{0,5} P_{H_2}^{0,5} + K_{H_2O} P_{H_2O} \right)} \quad (1.1)$$

$$r_2 = \frac{k_1 K_{CO_2} K_{H_2}^{0,5} \left(P_{CO_2} P_{H_2} - P_{CO} P_{H_2O} / K_{P2} \right) / P_{H_2}^{0,5}}{\left(1 + K_{H_2}^{0,5} P_{H_2}^{0,5} + K_{H_2O} P_{H_2O} \right) \left(1 + K_{CO_2} P_{CO_2} \right)} \quad (1.2)$$

where *k* – a constant of speed of corresponding reaction, *K* – a balance constant of corresponding substance, *P* – portion pressure of a corresponding component.

The model is made with the condition, that there is realized the mode of plug flow reactor in a catalyst layer. The choice of hydrodynamic model of ideal replacement is confirmed by high values of diffusive and thermal criteria a Scorching heat accepting in low-temperature synthesis, it is nearby 2000 [5]. With use of the industrial data from installation M-750 of synthesis of methanol, from “Sibmethakhim” Tomsk company, the mathematical model is checked on adequacy. To get this work done, there was comparison of concentration of key components of synthesis – methanol, hydrogen, carbonic and charcoal gases in a stream with results of laboratory analyses of installation. Also comparison of settlement and design concentration of components was done. The error of comparison doesn't exceed 12 % that will be coordinated with accuracy chromatography analysis. With use of the developed model the series of calculations directed on increase of productivity of installation without increasing the volume of the catalyst and processed gas has been spent. There has been designed the reactor of pre-catalysis for installation M-750, and calculated it’s optimum volume. It is shown that the optimum volume for catalyst in the reactor of a pre-catalysis equals 30 м^3. At such redistribution of volume of the catalyst, productivity of installation increases by 9,8 % without premature deactivation of the catalyst in the basic reactors.

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TUBULAR TURBULENT REACTOR IN THE PRODUCTION OF POLYISOPRENE IN THE LANTHANIDE CATALYST

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Catalytic systems based on lanthanide compounds are efficient catalysts for diene polymerization. A specific feature of these systems is high *cis*-stereospecificity, in particular, the polybutadiene and polyisoprene synthesized in the presence of these systems contain ~98% *cis*-1,4-units. Catalytic systems produced by the interaction of a lanthanide chloride and an organoaluminum compound are low-active in diene polymerization. The activity is significantly enhanced by adding electron-donor compounds to the catalyst. An electron-donor ligand increases the covalence of the lanthanide–halogen bond and thereby favors the alkylation of the lanthanide halide by the organoaluminum compound to form lanthanide–carbon bonds, which are active in polymerization. In this work we considered an unconventional way of enhancing the complexation of neodymium chloride with isopropyl alcohol in a single circulation of the reaction mixture through a turbulent flow reactor with convergent and divergent sections for synthesizing a highly active catalyst for stereospecific isoprene polymerization.

The initial reaction mixture contains $NdCl_3$ as particles ~15 µm in diameter. Within the first 4 h of mixing in the reaction the neodymium chloride particle size reduces to 4 µm. A further increase in the complexation process duration hardly influences the initial neodymium chloride particle size. The single circulation in turbulent reactor of the initial reactants during the formation of the reaction mixture crushes the neodymium chloride particles to a size that is characteristic of the suspension forming within 4–5 h in the synthesis. If the complexation complex duration exceeds 5 h, then the neodymium chloride particle size in any of the synthesis methods is ~4 µm. Analysis of the dynamics of the change in the $NdCl_3$ particle size and the accumulation of the complex $NdCl_3 \times 3IPA$ in the reaction mixture showed that the complexation is accelerated after reaching a certain particle size of the initial neodymium chloride. The short-term hydrodynamic action on the reaction mixture at the moment of its formation significantly increases the yield of the complex owing to the dispersion of the $NdCl_3$ particles.

Not only does changing the conditions of the synthesis of the alcohol solvate of neodymium chloride lead to the acceleration of the $NdCl_3$×3IPA accumulation in the reaction mixture, but also to a change in the dispersity of the end product. The most probable diameter of the $NdCl_3$×3IPA particles forming in the complexation is 110–125 nm. The short-term hydrodynamic action on the reaction mixture by method 2 gives rise to neodymium catalyst particles 50–65 nm in diameter. Obviously, the decrease in the $NdCl_3$ particle size under the hydrodynamic action is caused by an increase in the nucleation rate owing to an increase in the specific surface area of the initial neodymium chloride. It can be expected that a decrease in the $NdCl_3$×3IPA dispersity will increase the activity of neodymium catalytic systems in stereospecific isoprene polymerization.

The proposed method of the synthesis under the short-term hydrodynamic action at the moment of the formation of the reaction mixture leads to a noticeable decrease in the particle size of the end product of the complexation. This increases the neodymium catalyst activity in the stereoregular isoprene synthesis. The identified way of enhancing the neodymium catalyst production makes it possible to develop an energy- and resource-saving workflow of synthesis of gel-free polyisoprene using tubular turbulent reactors with convergent and divergent sections.

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MODELLING OF MOVING BED BIOFILM REACTORS FOR WASTEWATER TREATMENT

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The Moving Bed Biofilm Reactors (MBBR) [1,2] arose at the end of the last century in Norway emerging over other processes for biological wastewater treatment due to their attractive features. In these reactors the microorganisms grow attached to supports called "biomedias" that move freely through the reactor by the action of mechanical agitators in anoxic processes and due to aeration in the aerobic processes. Several authors [3,4,5] have reported numerous advantages of using MBBR's. The fact that the microorganisms are adhered on a support in the form of biofilm makes them more resistant to shock loading and dehydration. The biomedias have high surface area which provides high concentration of microorganisms within the reactor and the consequent improvement in the efficiency for pollutants removal. Given the permanence of the media inside the reactor, slow growing bacteria are favored, and thus the process of nitrification can be observed. Another advantage which may be mentioned is that the entire volume of the reactor is fully utilized due to the movement of the supports and that the amount of biomedias can be modified to improve the process. The importance of this reactor justify the development of mathematical models of this process, that can be used for scale up, process optimization, better understanding of the system, and helping predict possible behaviors. Thus, based on mathematical models from the literature [6,7,8,9], a different approach to model Moving Bed Biofilm Reactors is proposed in this paper, validated with experimental data. The model presented in this paper considers an aerobic process consisting in a three-phase system composed of a gaseous phase, a liquid phase and the biofilm. Part of the oxygen in the gas phase is transferred to the liquid phase and then penetrates the biofilm. Organic matter and nitrogen entering the reactor in the liquid phase also suffer from mass transfer to the biofilm, where all the metabolic reactions of consumption of pollutants occur. The microorganisms in the biofilm were separated into two groups, the autotrophic and heterotrophic, and considered homogeneously distributed. The first group of microorganisms is responsible for the consumption of ammonia and the second for the degradation of organic matter. The chemical reactions were included in the model according to Monod kinetics and the diffusion was described according to Fick's Law. The variation of thickness of the biofilm was modeled as a function of growth of microorganisms and of the detachment to the liquid phase. The software EMSO – Environment for Modeling, Simulation, Optimization and – was used for the dynamic process simulation using the method of orthogonal collocation for spatial discretization of the concentration profiles in the biofilm and the DASSLC solver for the time integration. Experimental data of Moving Bed Biofilm Reactors on the laboratory scale [10] was used to validate the mathematical model. The results obtained were satisfactory and the use of the proposed model proved very promising.

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ZIRCONIA-BASED COBALT CATALYSTS FOR FISCHER-TROPSCH SYNTHESIS

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Natural gas is a clean-burning and abundant energy resource, but much of it resides in locations remote from an economic means of transporting it to market. A logical solution for the problem would be to liquefy the natural gas, but this option requires very low temperatures and involves considerable costs. Another solution is to convert the natural gas into hydrocarbon liquids using chemical processing. Fischer-Tropsch technology allows to convert the natural gas into “syngas” (a mixture of carbon monoxide and hydrogen) followed by reaction to liquid fuels.[1]

FT synthesis has been considered as a part of gas-to-liquids (GTL) technology, which converts natural and associated gases to more valuable middle distillates and lubricants. In this technology, natural gas is first converted to syngas (carbon monoxide/hydrogen mixtures) via vapor reforming, partial oxidation or autothermal reforming. The reaction proceeds at 473–623 K and involves monometallic or bimetallic catalysts. Depending on catalyst (normaly cobalt or iron), reactor and conditions, FT synthesis could produce a wide range of hydrocarbons: light hydrocarbons, gasoline, diesel fuel and wax [2-4]. The hydrocarbons then undergo separation and further pretreatments such as hydrocracking and hydroisomerization. Therefore the catalyst is a vital part of any industrial FT process.

The catalysts were prepared by impregnating the carrier with an aqueous solution of cobalt nitrate and metal salts, promoters, and then air dried and calcined in a stream of air at 300 ° C. As the carrier has been used ZrO_2. Were prepared and tested the samples containing as promoters MgO, ZrO_2. The degree of reduction caused by cobalt, the magnitude of the active surface and the average size of its crystallites were determined using the oxygen titration. The degree of recovery of cobalt in the catalyst and So/ZrO_2 $So\text{-}ZrO_2/ZrO_2$ is 88% and 84%, which is high (whereas the degree of recovery is So/Al_2O_3 36%). The value of the active surface was low 1.97 m2 / g and 0.12 m2 / g, due to the large size of the crystallites co0 567 Å and 8870 Å. Introduction of the catalysts and So/ZrO_2 $So\text{-}ZrO_2/ZrO_2$ magnesium oxide resulted in a significant increase in the active surface of 10.5 m2 / g and an increase in dispersion Co from 1.8% and 0.1% to 11.3%, and 10, 4%. Thus, the introduction of the oxide MgO promoter contributes to greater growth of the active surface of the crystallites and the formation of smaller Co particles on the catalyst surface.

For the catalytic experiments at a pressure of 1 MPa using a laboratory flow-type setup with an integral reactor with a fixed catalyst bed. A mixture of CO and H_2 in a volume ratio of 1:2 having been used.

The most activity was shown on Co-ZrO_2-MgO/ZrO_2 catalyst with maximum CO conversion on it. Samples of Co/ZrO_2 and Co-ZrO_2/ZrO_2 were less active. The selectivity for methane reflects the most important side process occurring in the Co-catalysts in the Fischer-Tropsch synthesis. Lower selectivity to methane is a major problem in the SFT, as the methanation increased with temperature rise for all of catalysts. Maximum methane production was observed on Co/ZrO_2 and Co-ZrO_2/ZrO_2 catalysts, the selectivity of methane was 19, and 15%. At promoted MgO samples, the selectivity of methane was below the 9 and 7%. The target product of the synthesis of liquid hydrocarbons are C5 +. For all tested contact the optimum temperature of synthesis was about 230-240°C. The highest yield of liquid hydrocarbons was obtained on the Co-MgO/ZrO_2 and Co-ZrO_2-MgO/ZrO_2 contacts (119 and 133 missed g/nm3 gas, respectively).

Thus, the yields of liquid hydrocarbons for tested catalysts can be arranged in following order:

$$\text{Co-}ZrO_2\text{-MgO}/ZrO_2 > \text{Co-MgO}/ZrO_2 > \text{Co-}ZrO_2/ZrO_2 > \text{Co}/ZrO_2$$

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Peter Huber Kältemaschinenbau GmbH

Company Profile

Peter Huber Kältemaschinenbau GmbH is a leading manufacturer of high precision temperature control equipment from -120°C to +425°C for applications in laboratory, pilot plant and production. The company employs approximately 240 employees at its headquarters in Offenburg and operates internationally with offices and trading partners. More than 140,000 Huber temperature control products are in use in science, research and industrial applications. In 2011 for the third year in a row, Huber was awarded with the TOP 100 seal for being one of the 100 most innovative medium sized companies in Germany.

History

Huber Kältemaschinenbau was founded in 1968 as one of the first companies in refrigeration systems. master craftsmen and builders since 1984 GmbH in the family. With numerous product innovations, Huber has the technological development in the advanced liquid temperature.
A revolution in temperature control was the introduction of Unistat temperature control systems in 1989. To date, the tone is instantly when it comes to highly dynamic tempering processes. Typical applications are in the process and chemical engineering, semiconductor industry, solar technology, material testing and chemical and pharmaceutical research. In addition to the temperature control systems of the Unistat series, the product range offers chillers and classical heating and cooling thermostats.

Products

The Huber product range offers solutions for all temperature applications from -120°C to +425 °C. The range includes high performance temperature control with cooling capacities up to 250 kW as well as classic chillers and heating and cooling thermostats.

Dynamic Temperature Control Systems – Unistat, Tango, Petite Fleur

Huber Unistat offer unmatched thermodynamics and advanced control technology.

- Efficient heating and cooling technology
- Short heating and cooling
- Wide temperature range with no fluid exchange
- More than 60 models with cooling of 0.7 to 130 kW

Heating and Cooling Thermostats – Compatible Control, MPC, Ministat, Variostat

The Huber thermostat program written to model a wide range of temperatures from -90 ° C to +300 ° C.

- Hook-and bridge thermostats
- baths with polycarbonate or stainless steel baths
- Circulators for external temperature
- Refrigeration and Low Refrigerated Circulators
- Over 70 models with cooling capacities up to 7 kW

Chiller – Unichiller, Minichiller, RotaCool

Huber Minichiller and Unichiller offer environmentally friendly and economic cooling solutions.

- Environmentally friendly alternative to cooling with fresh water
- Small size, high performance
- Rugged stainless steel construction
- Proven, reliable technology life
- Over 50 models with cooling capacities from 0.3 to 50 kW

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Temperature control of production reactors

Improvement of heating and cooling systems in chemical production

The Unistat Hybrid system is capable of controlling the temperature of production reactor volumes of up to 10,000 l or more

Precise temperature control has a significant influence on performance and quality in chemical process engineering. The Unistat range of temperature control systems ensure, accurate temperatures and stable process conditions in research laboratories, pilot plants and kilolabs worldwide. The new Unistat Hybrid technology from Huber, offers solutions for temperature control of large scale production reactors, enabling an affordable partial modernisation of existing central plant cooling/heating systems.

When it comes to chemical reactions in production processes the right temperature is critical and so accordingly, is the need for an appropriate heating/cooling solution. For process engineers it is essential to find a compromise between yield quality and productivity. Over the years, and with the support of process engineers from the chemical and pharmaceutical industry, the Unistat range has been developed and refined. This collaboration has ensured that Unistats remain at the forefront of technology, making them suitable for controlling the temperature of chemical and bioreactors, autoclaves, miniplants and pilotplants, reactor blocks ,calorimeter and distillation plants. As a result of their thermodynamic characteristics, Unistats offer cutting edge performance regardless of the application.

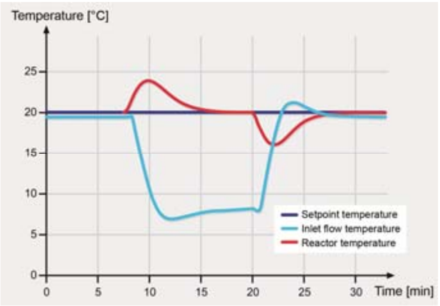
The Unistat concept guarantees reliable operation with stable process conditions and precise results, offering several functions and settings to aid fine adjustment of the application, for example, TAC temperature control. TAC (True Adaptive Control) analyses the controlled fluid circuit, and constantly adjusts the control parameters ; resulting in precise control with minimum effort for the user. These settings and outstanding thermodynamics allow Unistats to excel, even under heavily changing system conditions. To demonstrate the performance of the Unistat range over 200 case studies have been created to show the Unistats unique ability to adapt to process requirements, offering precise stability and control.

Fig. 1: The Unistat Hybrid System is capable of controlling the temperature of production reactor volumes of 10,000 litres or more. The advantages of the Unistat Hybrid are highly precise thermoregulation and fast, reliable control of thermal reactions.

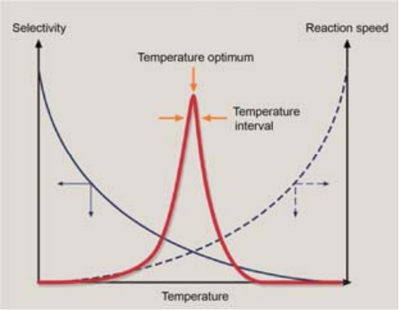
More than 50 models for process engineering

Over 50 models are available as standard in the Unistat product group suiting every application. They range from very compact units to powerful models (fig. 2) for controlling temperature of production reactors up to approximately 1,000 litres or more, depending on the application. The temperature range of the Unistats is from -120 °C to +425 °C with cooling capacities of 150 kW. In addition Unistats can be custom built to fit individual application requirements.

Unistats stand out in safety and economy! The efficient energy management system keeps electrical power consumption to a minimum. Reduced operating costs and minimal use of water further saves on utility consumption. The hydraulically sealed construction of the Unistat range prevents the formation of oil vapours and oxidation, extending the lifetime of costly thermal fluids by years. The Unistat Pilot offers comprehensive safety features and continuously monitors the process allowing Unistats to run remotely. In the event of an emergency, alarms are activated and, depending on the user defined settings, the system will then either turn off, or the emergency over-temperature protection function will be activated; switching the machine to 100% cooling in the event of a thermal runaway. Further features such as: the programmer, adaptive cascade control, ramp functions, calendar start, individual user menus, sensor calibration and analogue and digital interfaces for integration in process control systems round off the Unistats functionality.



Fast and reliable stability of temperature with exothermic reactions



Temperature has a major influence on selectivity and reaction time

In addition options for weather protection and/or winter operation are available, allowing units to be located outdoors and controlled remotely. For Unistats sited in ATEX zones 1 & 2, Huber offers two solutions. The Unistat can either be placed in an Ex-p pressure chamber or an ATEX certified controller can be mounted in the ATEX area whilst the Unistat remains in the safe zone.

Temperature control of production reactors with more than 10 m³
The introduction of the new Unistat Hybrid technology extends the range of Huber systems allowing temperature control of large volume reactors of 10,000 litres or more. The Unistat Hybrid combines the precise control of the Unistat range, with the power of existing energy resources in a production facility such as steam, cooling water or liquid nitrogen (fig. 3), offering powerful process control and a partial cost effective modernisation of existing resources.
Using a Unistat Hybrid system in this way, allows the Unistat to manage the interaction of the individual energy sources and control temperature accordingly. This results in faster heating times for large volume reactors heated by steam (fig. 6) or respectively faster cooling times with liquid nitrogen or cooling water. The advantages of this technique are precise control, an extended temperature range, more heating and cooling power and reliable control of thermal reactions. Linking the Unistat Hybrid into an existing centralised cooling/heating system results in better process conditions and improved production output.

Steam from production plants is used for thermal control of reactors: the Unistat Hybrid temperature control system and external eat exchanger unit are connected to the reactor jacket

Fig. 3: Complete solution: The Unistat Hybrid temperature control system with external heat exchangers for the various energy sources (steam, cooling water, liquid nitrogen) provides optimum interaction.

Fig. 4: Fast and reliable stability of temperature with exothermic reactions
Fig. 5: Temperature has a big influence on selectivity and reaction time.

Professional Scale-up
The Unistat product range offers temperature control solutions for nearly all applications in chemical process engineering. There are over 50 air and water cooled models to choose from, with cooling powers from 0.7 kW to 150 kW for temperatures from -120 °C to +425 °C. Additionally a wide assortment on accessories is offered for example: sensors, thermal fluids, hose connections, ATEX solutions as well as service agreements and certificates. Unistats provide professional scale-up offering the same stable process conditions from development lab, pilot plants to production systems.

Fig. 6: Using steam from production plants for thermal control of reactors. The Unistat Hybrid temperature control system and external heat exchanger unit (right figure) is connected to the reactor jacket.

Modernisation of plants with the Unistat Hybrid
Large scale pharmaceutical and chemical manufacturing plants traditionally use a centralised system of heating and cooling to control temperature of production processes.
The Unistat Hybrid allows improvements of existing temperature control solutions by linking them with a hydraulically sealed temperature control system.
The Unistat Hybrid system increases the present cooling and heating power and expands the temperature range.

Advantages

- Greater heating and cooling power
- Utalises existing resources; such as steam, cooling water, liquid Nitrogen etc.
- Wider temperature range for existing systems
- Highly accurate control of the process temperature
- Reliable control of thermal reactions
- Reasonably priced modernisation of existing systems
- Minimises expensive and time consuming system replacements

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